3-Chloro-2-[(diethoxyphosphoryl)oxy]-1-propene: A New Reagent for a "One-Pot" Cyclopentenone Annelation. Syntheses of Desoxyallethrolone, *cis*-Jasmone, and Methylenomycin B

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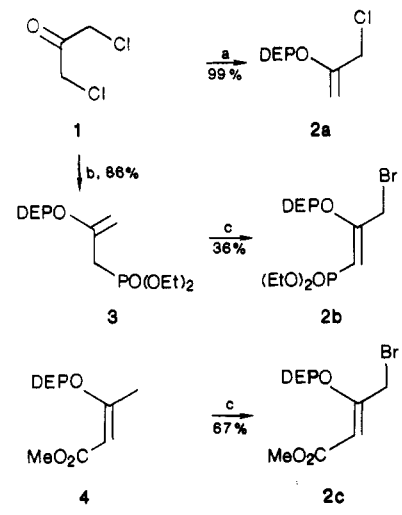
A new reagent, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**), for the preparation of cyclopentenones from ketone precursors via a "one-pot" synthesis is described. Alkylation studies of **2a** and other enol phosphate based electrophiles **2b** and **2c** with various nucleophiles is discussed. The application of reagent **2a** to the synthesis of desoxyallethrolone (**11**), *cis*-jasmone (**14**), and methylenomycin B (**21**) is presented.

The biological importance and tremendous diversity of cyclopentanoid natural products have made these compounds important synthetic goals and have stimulated the development of new methods and reagents for the preparation of cyclopentenone rings. Several reviews have appeared in the literature that document the technology used in the construction of cyclopentenone rings.[1] A well-established strategy for the synthesis of cyclopentenones is the intramolecular aldol condensation of 1,4-diketones. The latter generally are available by carbon–carbon bond forming reactions between C_3 synthons ($CH_3COCH_2^+$) and ketone enolate or imine anion or enamine precursors. Nearly all of these known C_3 synthons used in the preparation of cyclopentenones require three separate and distinct synthetic steps: (1) alkylation; (2) hydrolysis or oxidation; and (3) intramolecular aldol condensation.[2] The purpose of this paper is to present the full details of a new reagent, **2a** (Scheme I), for a "one-pot" cyclopentenone annealation based upon enol phosphate chemistry.[2o] Reagent **2a** is easily prepared from readily available and inexpensive starting materials. Reagent **2a** also is stable to storage for months at 23 °C and years at 5 °C with the exclusion of moisture.

The chemistry of enol phosphates has been reviewed.[3] Enol phosphates are hydrolyzed by C–O fission with dilute HCl or H_2SO_4 in EtOH/H_2O at reflux or with P–O fission with dilute KOH or NaOH in H_2O at reflux with reasonably short half-lives. In the case of base cleavage, the resulting diethyl phosphate anion [$(EtO)_2PO_2^-$ = DEPO$^-$] is resistant to further hydrolysis or nucleophilic attack and the corresponding enolate anions are free to undergo intramolecular aldol condensations.

Scheme I[a]



[a] (a) $(EtO)_3P$, 100 °C; (b) $(EtO)_3P$, 160 °C; (c) NBS, AIBN, CCl_4, $h\nu$.

The new reagent, 3-chloro-2-[(diethoxyphosphoryl)-oxy]-1-propene (**2a**), is prepared in near quantitative yield from equivalent amounts of 1,3-dichloroacetone and triethyl phosphite at 40–100 °C via a Perkow reaction[4] (see Scheme I). If 2 equiv of triethyl phosphite are used with 1 equiv of 1,3-dichloroacetone at 160 °C, then enol phosphate–phosphonate **3** is formed in 86% yield.[5] Allylic bromination of **3** or **4**[6] with *N*-bromosuccinimide and a catalytic amount of azobis(isobutyronitrile) in CCl_4 affords **2b** in 36% yield or **2c** in 67% yield, respectively.[7]

The electrophilic character of reagents **2a**, **2b**, and **2c** was extensively explored with a variety of nucleophiles (see Table I for the details). In summary, the carbon–carbon bond forming reactions between enolate anions of β-keto esters and reagents **2a**, **2b**, and **2c** proceed in good to excellent yields as shown in entries 2, 3, 4, and 10–14 of Table I. In one case, entry 2, hexamethylphosphoric triamide dramatically improved the yield of the alkylation product. Alkylation of **2a** with the lithium enolate anion of cyclohexanone proceeds in a modest 65% yield in THF; however, if the reaction is conducted in the presence of 5

(1) (a) Ellison, R. A. *Synthesis* **1973**, 397. (b) Ho, T.-L. *Synth. Commun.* **1974**, *4*, 265; *Ibid.* **1977**, *7*, 351. (c) Paquette, L. A. *Tetrahedron* **1981**, *37*, 452. (d) Trost, B. M. *Chem. Soc. Rev.* **1982**, 141. (e) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820. (f) Ramaiah, M. *Synthesis* **1984**, 529. (g) Yoshikoshi, A.; Miyashita, M. *Acc. Chem. Res.* **1985**, *18*, 284. (h) Paquette, L. A. *Aldrichimica Acta* **1984**, *17*, 43. (i) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(2) Selected references for cyclopentenone reagents: (a) Piers, E.; Abeysekera, B. *Can. J. Chem.* **1982**, *60*, 1114. (b) Begley, M. J.; Cooper, K.; Pattenden, G. *Tetrahedron* **1981**, *37*, 4503. (c) Aristoff, P. A. *Synth. Commun.* **1983**, *13*, 145. (d) Trost, B. M.; Curran, D. P. *J. Org. Chem.* **1980**, *45*, 5699. (e) Jacobson, R. M.; Raths, R. A.; McDonald, J. H., III. *J. Org. Chem.* **1977**, *42*, 2545. (f) Hosomi, A.; Shirahata, A.; Araki, Y.; Sakurai, H. *J. Org. Chem.* **1981**, *46*, 4631. (g) Tsuji, J.; Yamada, Y.; Shimizu, I. *J. Org. Chem.*, **1980**, *45*, 5209. (h) Martin, S. F.; Chou, T. *J. Org. Chem.* **1978**, *43*, 1027. (i) Islam, A. M.; Raphael, R. A. *J. Chem. Soc.* **1952**, 4086. (j) Stork, G.; Jung, M. E.; Calvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684. (k) Klipa, D. K.; Hart, H. *J. Org. Chem.* **1981**, *46*, 2815. (l) Miyashita, M.; Yanami, T.; Kumazawa, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1984**, *106*, 2149. (m) DeBorer, A.; Eilwanger, R. *J. Org. Chem.* **1974**, *39*, 77. (n) Schuda, P. F.; Bernstein, B. *Synth. Commun.* **1984**, *14*, 293. (o) Welch, S. C.; Assercq, J.-M.; Loh, J.-P. *Tetrahedron Lett.* **1986**, *26*, 1115.

(3) (a) Lichtenthaler, F. W. *Chem. Rev.* **1961**, *61*, 607. (b) Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415.

(4) Allen, J. F.; Johnson, O. H. *J. Am. Chem. Soc.* **1955**, *77*, 2871. Usually commercially available technical grade 1,3-dichloroacetone is used; however, it can be prepared from the following procedures: (a) Conant, J. B.; Quayle, O. R. *Organic Syntheses*; Wiley: New York, 1964; Collect. Vol. 1, 211; (b) Conant, J. B.; Quale, O. R. *Organic Syntheses*; Wiley: New York, 1964; Collect. Vol. 1, 292.

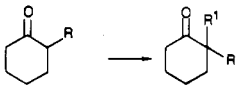
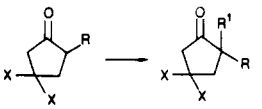
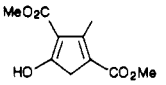
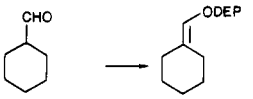
(5) Jacobson, H. I.; Griffin, M. J.; Preis, S.; Jensen, E. V. *J. Am. Chem. Soc.* **1957**, *79*, 2608.

(6) Sum, F.-W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431.

(7) Welch, S. C.; Gruber, J. M. *J. Org. Chem.* **1982**, *47*, 385.

0022-3263/87/1952-1440$01.50/0

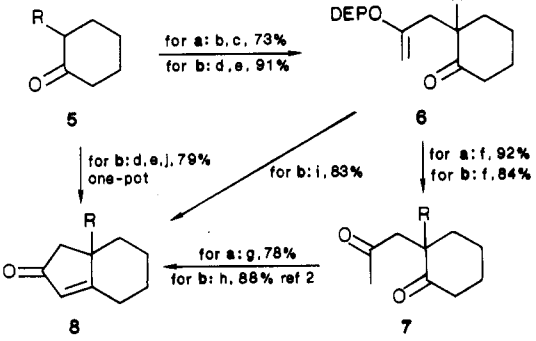
Table I

entry	alkylating agent	starting materials	base/solvent/cat.	product[a]	yield, %
					
1.	2a	R = CO_2Me	KH/THF	R^1 = A, R = CO_2Me	27
2.	2a	R = CO_2Me	KH/THF/HMPA	R^1 = A, R = CO_2Me	73
3.	2b	R = CO_2Me	NaH/THF/5% $(Ph_3P)_4Pd$	R^1 = B, R = CO_2Me	58
4.	2c	R = CO_2Me	NaH/THF	R^1 = C, R = CO_2Me	90
5.	2a	R = H	1.1 equiv LDA/THF	R^1 = A, R = H	65
6.	2a	R = H	1.1 equiv LDA/THF 5% $(Ph_3P)_4Pd$	R^1 = A, R = H	91
7.	2b	R = H	1.1 equiv LDA/THF	R^1 = B, R = H	13
8.	2b	R = H	1.1 equiv LDA/THF 5% $(Ph_3P)_4Pd$	R^1 = B, R = H	10
9.	2c	R = H	1.1 equiv LDA/THF	R^1 = C, R = H	15
					
10.	2a	X = CH_3, R = CO_2Me	NaH/THF	X = CH_3, R^1 = A, R = CO_2Me	60
11.	2a	X = H, R = CO_2Me	NaH/THF	X = H, R^1 = A, R = CO_2Me	76
12.	2a	$CH_3COCH_2CO_2Me$	NaH/THF	$CH_3COCH(A)CO_2Me$	67
13.	2a	$CH_3COCH_2CO_2$-*t*-Bu	NaH/THF	$CH_3COCH(A)CO_2$-*t*-Bu	59
14.	2c	$CH_3COCH_2CO_2Me$	NaH/THF		65[b]
15.	2a	CH_3CO_2-*t*-Bu	1.1 equiv LDA/THF 5% $(Ph_3P)_4Pd$	ACH_2CO_2-*t*-Bu	57
					
16.	2a		KH/THF		64
17.	2a		KH/THF/5% $(Ph_3P)_4Pd$		60
18.	2a		Ph_3CK/DME		31

[a] A = $CH_2C(ODEP)=CH_2$; B = $CH_2C(ODEP)=CHPO(OEt)_2$; C = $CH_2C(ODEP)=CHCO_2Me$. [b] After quench with NH_4Cl, H_2O.

mol % of $(Ph_3P)_4Pd$ in THF, the yield substantially increases to 91%. Negishi and co-workers have demonstrated that $(Ph_3P)_4Pd$ enhances the reactivity of electrophiles in such alkylation reactions.[8] Unfortunately, compounds **2b** and **2c** undergo alkylation with the lithium enolate anion of cyclohexanone under similar conditions in rather poor yields (10–15%). The lithium enolate anion of *tert*-butyl acetate[9] reacts with **2a** in the presence of a catalytic amount of $(Ph_3P)_4Pd$[8] in THF to afford the respective alkylated product in 57% yield (entry 15 of Table I). Treatment of the potassium enolate anion of cyclohexanecarboxaldehyde under a variety of conditions[10] affords only the enol phosphate ester of the starting aldehyde (entries 16–18 of Table I). The reaction of **2a**, **2b**, or **2c** with enamines[11] or imine anions[12] proceeded in zero to very poor yields. Despite these limitations, the possibility of using reagent **2a** as an cyclopentenone annelating agent was explored further.

Scheme II[a,b]

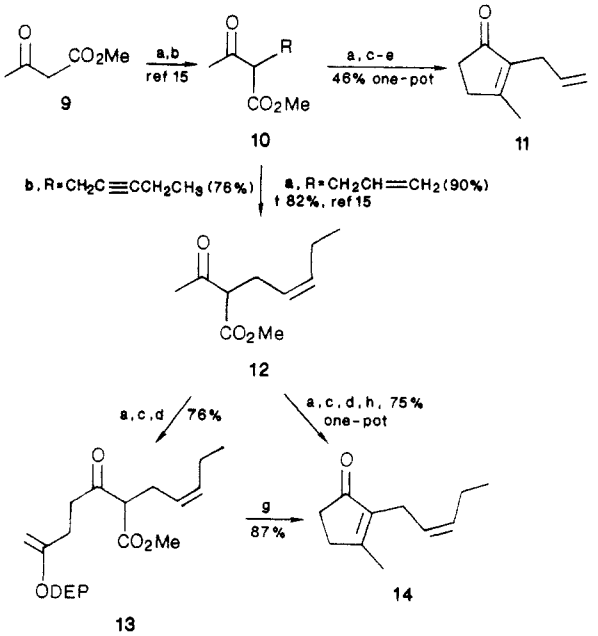


[a] DEP = $(EtO)_2PO$. **a**, R = CO_2Me; **b**, R = H. [b] (b) KH, THF, HMPA; (c) 2; (d) 1.1 equiv LDA, THF; (e) 2, 5% $(Ph_3P)_4Pd$, THF; (f) 10% HCl, acetone, reflux 3 h; (g) NaH, $PhCH_3$, reflux 10 h; (h) 5% KOH, H_2O, reflux 6 h; (i) 5% KOH, H_2O, reflux 8.5 h; (j) 10% NaOH, H_2O, EtOH, reflux, 24 h.

Scheme II details the model reactions that were investigated in an effort to develop reagent **2a** into a cyclopentenone annelating agent. This application of reagent **2a** was explored with 2-carbomethoxycyclohexanone (**5a**, R = CO_2Me) and cyclohexanone (**5b**, R = H). Alkylation

(8) (a) Negishi, E.; Luo, F.-T. *J. Org. Chem.* **1983**, *48*, 2427. (b) Negishi, E.; John, R. A. *J. Org. Chem.* **1983**, *48*, 4098.
(9) Rathke, M. W.; Sullivan, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 3050.
(10) (a) Groenewegen, P.; Kallenberg, H.; Van der Gen, A. *Tetrahedron Lett.* **1978**, 491. (b) Huffman, J. W.; Harris, P. G. *J. Org. Chem.* **1977**, *42*, 2357.
(11) (a) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuskovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207. (b) Chatterjee, A. *Tetrahedron Lett.* **1965**, *26*, 959.
(12) (a) Stork, G.; Dowd, S. *J. Am. Chem. Soc.* **1963**, *85*, 2178. (b) Wittig, G.; Frommeld, H. D.; Suchanek, P. *Angew. Chem.* **1963**, *75*, 978.

Scheme III. Syntheses of Desoxyallethrolone and *cis*-Jasmone[a]



[a] (a) NaH, THF; (b) $BrCH_2CH{=}CH_2$ or $BrCH_2C{\equiv}CCH_2CH_3$; (c) *n*-BuLi, hexane; (d) **2a**, (e) 10% NaOH, H_2O, 50 °C, 12 h; (f) 1 equiv H_2, MeOH, 5% $Pd/BaSO_4$, quinoline; (g) 3% NaOH; H_2O, THF, 80 °C, 20 h; (h) 20% NaOH, H_2O, reflux, 65 h.

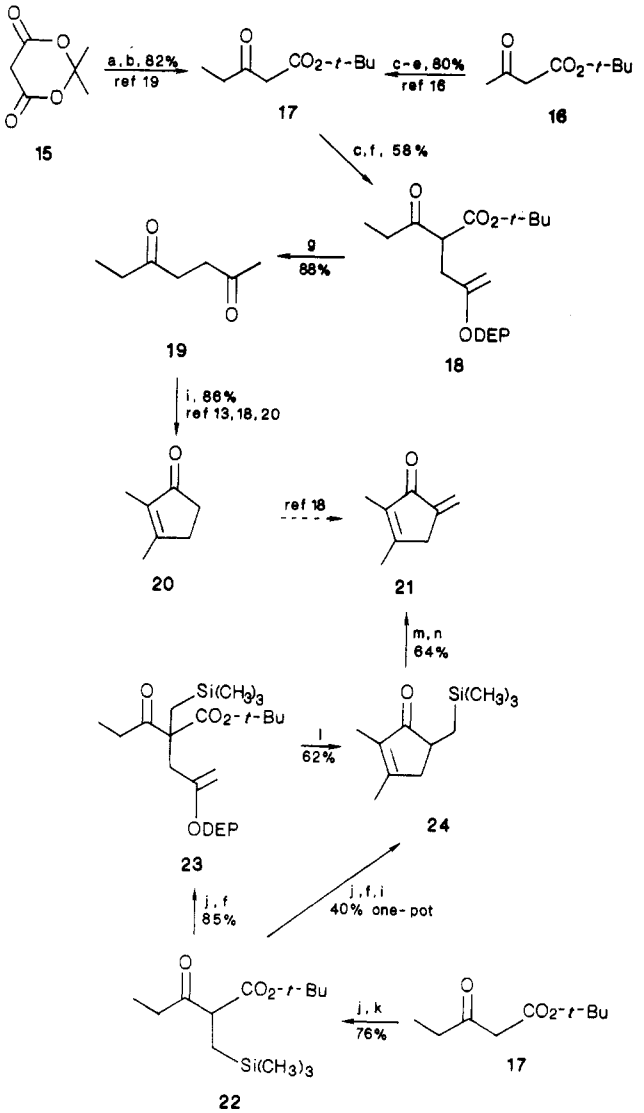
of β-keto ester **5a** by generation of the enolate anion with potassium hydride in THF/HMPA followed by the addition of **2a** affords **6a** in 73% yield. Generation of the enolate anion of ketone **5b** with 1.1 equiv of lithium diisopropylamide (LDA) in THF followed by the addition of **2a** in THF containing 5 mol % of $(Ph_3P)_4Pd$ catalyst produces **6b** in 91% yield.[8] The latter reaction proceeded in only 65% yield in the absence of the $(Ph_3P)_4Pd$ catalyst.[5]

Hydrolysis of enol phosphates **6a** or **6b** with 10% HCl in acetone/H_2O at reflux for 3 h gives diketones **7a** or **7b** in 92% or 84% yields, respectively. Intramolecular aldol condensation of **7a** with NaH in refluxing $PhCH_3$ for 19 h affords **8a** in 78% yield.[2] Cyclization of diketone **7b** with 5% KOH in H_2O at reflux for 6 h produces **8b** in 88% yield.[2] Concomitant hydrolysis and intramolecular aldol condensation of **6b** to **8b** in 83% yield was carried out with 5% KOH in H_2O at reflux for 8.5 h. Other bases (KOH/EtOH or KOEt/EtOH) proved to be less efficient. Finally, the one-pot cyclopentenone annelation process was conducted as follows: The enolate anion of cyclohexanone (**5b**) was generated with 1.1 equiv of LDA in THF followed by the addition of **2a** in THF containing 5 mol % of $(Ph_3P)_4Pd$, then quenching with 10% NaOH in EtOH/H_2O and heating at reflux for 24 h affords **8b** (R = H) in 79% overall yield from **5b** (R = H). This latter experiment thus demonstrates the usefulness of reagent **2a** as a one-pot cyclopentenone annelating agent.

Scheme III shows the application of reagent **2a** in the "one-pot" syntheses of desoxyallethrolone (**11**) and *cis*-jasmone (**14**).[13,16] The synthesis of desoxyallethrolone (**11**) is of interest because it is a potential starting material in the preparation of allethrolone and pyrethrins.[13] The synthesis of *cis*-jasmone (**14**) is noteworthy because of the value of *cis*-jasmone (**14**) in perfumery.[1b,14] Alkylation of methyl acetoacetate (**9**) under standard conditions (NaH/THF) with allyl bromide or 1-bromo-2-pentyne affords compound **10a** or **10b** in 90% or 76% yields, respectively.[15] Generating the dianion of **10a** with NaH/THF followed by the addition of 1 equiv of *n*-BuLi/hexane and subsequent alkylation with **2a** and treatment with 10% NaOH/H_2O at 50 °C for 12 h produces desoxyallethrolone (**11**) in 46% overall yield in a one-pot process.

Catalytic hydrogenation of **10b** over 5% $Pd/BaSO_4$ in MeOH/quinoline gives **12**.[15] Generation of the dianion of **12** with NaH/THF followed by 1 equiv of *n*-BuLi/hexane and quenching with **2a** affords **13** in 76% yield.[15] Treatment of **13** with 3% NaOH/H_2O/THF at 80 °C for 20 h gives *cis*-jasmone (**14**) in 87% yield. The one-pot process for the synthesis of *cis*-jasmone (**14**) from **12** proceeds in 75% overall yield as follows: generation of the dianion of **12** with NaH/THF followed by the addition of 1 equiv of *n*-BuLi/hexane and then alkylation with **2a** and subsequent treatment with 20% NaOH/H_2O at reflux for 65 h gives *cis*-jasmone (**14**) in 75% overall yield.[15,16]

Scheme IV. Syntheses of Methylenomycin B[a]



[a] (a) CH_3CH_2COCl, py, CH_2Cl_2; (b) *t*-BuOH, C_6H_6, reflux, 3 h; (c) NaH, THF; (d) *n*-BuLi, hexane; (e) CH_3I; (f) **2a**; (g) 10% H_2SO_4, EtOH, reflux, 72 h; (h) 20% H_2SO_4, EtOH, reflux 72 h; (i) 2% NaOH, EtOH, reflux 8 h; (j) NaH, dioxane, HMPA; (k) $(CH_3)_3SiCH_2I$; (l) 2% NaOH, EtOH, 96 h; (m) 2 equiv Br_2, CCl_4, 0 °C; (n) Zn, HOAc, Et_2O.

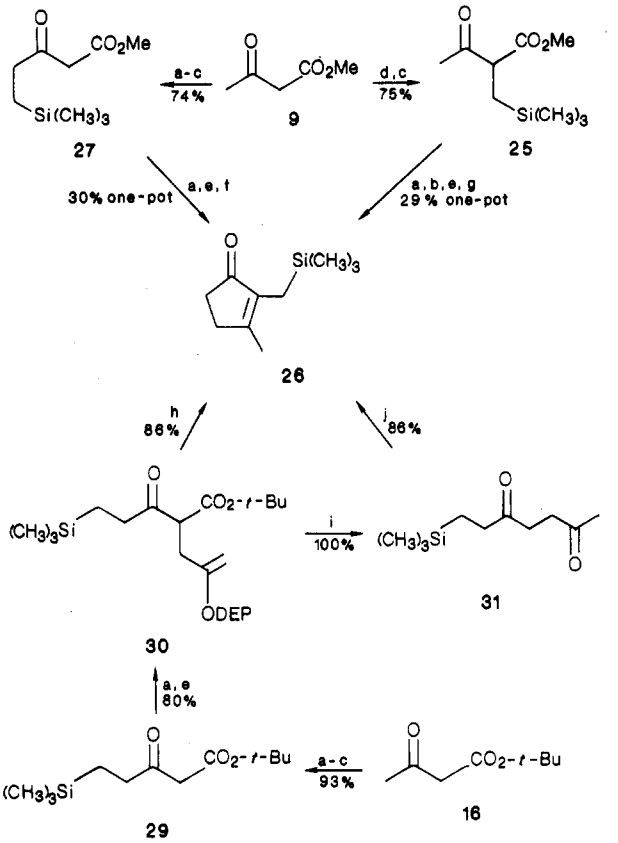
(13) (a) Piers, E.; Cheng, K. F.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 1256. (b) Romanet, R. F.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 3701.
(14) Rosini, G.; Ballini, R.; Sorrenti, P. *Tetrahedron* **1983**, *39*, 4127.
(15) Sum, P. E.; Weiler, L. *Can. J. Chem.* **1978**, *56*, 2301.
(16) Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

Scheme IV displays two approaches to the synthesis of methylenomycin B (**21**). Methylenomycin B (**21**) is reported to be an unstable antibiotic molecular isolated from *Streptomyces violacesruber*.[17] Several previous syntheses of methylenomycin B have been reported.[18] Both of our approaches to antibiotic **21** begin with β-keto ester **17** which is available from either Meldrum's acid (**15**) or *tert*-butyl acetoacetate (**16**). Treatment of Meldrum's acid (**15**) with propionyl chloride in CH_2Cl_2/py followed by *tert*-butyl alcohol in benzene at reflux affords β-keto ester **17** in 82% overall yield.[19] Alternatively β-keto ester **17** can be prepared in 80% yield by alkylation of the dianion of *tert*-butyl acetoacetate (**16**).[16] Generation of the monoanion of **17** with NaH/THF and addition of **2a** produces compound **18** in 58% yield. Hydrolysis and concomitant decarboxylation of compound **18** with 10% H_2SO_4/EtOH at reflux for 72 h gives diketone **19**. Intramolecular aldol condensation of diketone **19** with 2% NaOH/EtOH at reflux for 8 h affords 2,3-dimethylcyclopentenone (**20**) in 86% yield.[13a,18,20] The latter ketone has been previously transformed to methylenomycin B.[18]

The second synthesis of methylenomycin B shown in Scheme IV begins with β-keto ester **17**.[16,19] Generation of the monoanion of compound **17** with NaH/dioxane/HMPA followed by the addition of (iodomethyl)trimethylsilane produces β-keto ester **22** in 76% yield. Generation of the monoanion of compound **22** with NaH/dioxane/HMPA followed by quenching with **2a** gives product **23** in 85% yield. Treatment of compound **23** with 2% NaOH/EtOH at reflux for 4 days affords cyclopentenone **24** in 62% yield by concomitant hydrolysis, decarboxylation, and intramolecular aldol condensation. Finally, cyclopentenone **24** was allowed to react with 2 equiv of bromine in CCl_4 at 0 °C to give a dibromide intermediate. The latter was reduced with zinc in HOAc/Et_2O to produce methylenomycin B (**21**) in 64% overall yield.[21]

Scheme V displays four different synthetic approaches to 2-[(trimethylsilyl)methyl]-3-methylcyclopent-2-en-1-one (**26**).[22] Ketone **26** was of interest because of the potential utility of it in the possible construction of tricyclic cyclopentanoid natural products via Trost-type annelations.[1] Alkylation of the monoanion of methyl acetoacetate (**9**) with (iodomethyl)trimethylsilane in dioxane/HMPA produces β-keto ester **25** in 75% yield. Generation of the dianion of β-keto ester **25** with (1) NaH/THF and (2) *n*-BuLi/hexane followed by the addition of **2a** and conditions for a one-pot cyclization (1.3% NaOH/H_2O reflux) affords enone **26** in 29% overall yield. Alkylation of the dianion[16] of methyl acetoacetate (**9**) with (iodomethyl)-trimethylsilane gives β-keto ester **27**. Alkylation of the monoanion of β-keto ester **27** with **2a** followed by a one-pot annelation (10% NaOH/H_2O/reflux) produces enone **26** in 30% overall yield. A more efficient approach to enone **26** begins with *tert*-butyl acetoacetate (**16**). Generation of the dianion of β-keto ester **16** with (1) NaH/THF and (2) *n*-BuLi/hexane followed by quenching with (iodomethyl)trimethylsilane affords β-keto ester **29** in 93% yield. Alkylation of the monoanion of β-keto ester **29** with **2a** gives compound **30** in 80% yield. Treatment of compound **30** with 20% H_2SO_4/EtOH at reflux for 72 h produces cyclopentenone **26** in 86% yield. Alternatively, β-keto ester **30** can be hydrolyzed with 20% H_2SO_4/acetone for 72 h to afford diketone **31** in quantitative yield. Intramolecular aldol condensation of diketone **31** with 2% NaOH/H_2O at reflux for 8 h gives cyclopentenone **26** in 86% yield.

Scheme V. Synthesis of 2-[(Trimethylsilyl)methyl]-3-methylcyclopent-2-en-1-one[a]



[a] (a) NaH, THF; (b) *n*-BuLi, hexane; (c) $(CH_3)_3SiCH_2I$; (d) NaH, dioxane, HMPA; (e) **2a**; (f) 10% NaOH, H_2O, H_2O, reflux; (g) 1.3% NaOH, H_2O reflux; (h) 20% H_2SO_4, EtOH, reflux, 72 h; (i) 20% H_2SO_4, acetone, reflux, 72 h; (j) NaOH, EtOH, reflux, 8 h.

In conclusion the new cyclopentenone annelating reagent **2a** is easily prepared and storable for months. Reagent **2a** undergoes alkylation with a variety of nucleophiles and it can be used in a one-pot synthesis of cyclopentenones.

Experimental Section

Materials and Techniques. Melting points were determined on a Buchi capillary melting point apparatus. "Bulb-to-bulb" distillation refers to horizontal short-path distillation in which the crude material was heated in a Buchi Kugelrohr oven. The temperature of the air chamber during distillation is reported as the boiling point. All melting points and boiling points are uncorrected and reported in degrees Celsius. Combustion analyses were performed by Spang Microanalytical Laboratory. Silica gel 60 HF 254–366 (E. Merck No. 7741) or silica gel 60 F_{254} pre-coated TLC sheets (E. Merck No. 7734, 70–230 mesh) was used for gravity column chromatography. Medium-pressure liquid chromatography[23] was performed on a chromatograph equipped with a Fluid

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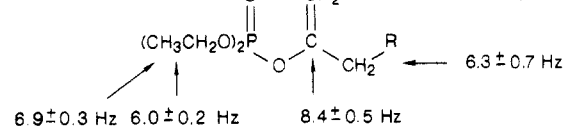
Metering lab pump Model RPSYX, a pulse dampener (Fluid Metering), and Altex repackable columns packed with silica gel 60 (230–400 mesh, E. Merck No. 9385) available from Brinkmann Instruments. Analytical gas-phase chromatography (GLC) was performed on a Varian Aerograph Model 1400 equipped with a flame-ionization detector with He as the carrier gas and using the following types of columns and flow rates: (a) 6 ft, stainless steel, $^1/_8$ in. column packed with 5% OV-17 on Varaport 20 (80/100 mesh, Varian), flow rate 15 mL/min; (b) 6 ft, stainless steel, $^1/_8$ in. column packed with 5% SE-30 on Varaport 30 100/120 mesh, flow rate 15 mL/min; (c) 5 ft, stainless steel, $^1/_8$ in. column packed with 5% FFAP on 60/80 Gas Chrom P, flow rate 15 mL/min. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 237B spectrometer. Samples were dissolved in spectroquality CCl_4 (10% solution) and spectra were taken using 0.1-mm NaCl solution cells. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates Model T-60 or on a Varian Model FT-80 spectrometer using spectroquality $CDCl_3$. Low-resolution mass spectra were recorded at 70 eV on a Hewlett-Packard spectrometer Model 5930A with gs chromatograph (Model 5710) and data system (Model 5933A). The titre of commercially available (Aldrich Chemical Company) *n*-butyllithium was determined by the methods of Watson[24] or Jones and Gilman.[24] Ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from $LiAlH_4$ under nitrogen just prior to use. Carbon tetrachloride, when used as a reaction solvent, was distilled from P_2O_5. Diisopropylamine and *tert*-butyl alcohol were distilled from CaH_2 (–40 mesh). Hexamethylphosphoric triamide (HMPA) was vacuum distilled from calcium hydride (–40 mesh) onto freshly activated molecular sieves (type 13X). Dioxane was purified by distillation from sodium/benzophenone followed by a second distillation from $LiAlH_4$. For all reactions performed under nitrogen, the glassware was dried in an oven at 120 °C for several hours and then allowed to cool in a dessicator. All liquid transfers were made with nitrogen-flushed syringes. Sodium hydride (61.1% in oil, Ventron) and KH (24% in oil, Ventron) were washed with anhydrous Et_2O (3×) under N_2 and the remaining Et_2O was removed under vacuum or with a stream of N_2 prior to use.

The following are the ^{13}C–^{31}P coupling constants observed for the alkylated products prepared herein:



3-Chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (2a). A 50-mL, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen inlet, and a magnetic stirring bar was charged with 1,3-dichloroacetone[4] (5.93 g, 44.4 mmol). The solid was warmed to 40 °C and triethyl phosphite (9.5 mL, 44.4 mmol) was syringed into the flask, under vigorous stirring, at such a rate that the temperature was maintained between 40 and 50 °C. The reaction mixture was then stirred for 1 h at 60 °C, 1 h at 80 °C, and then 1 h at 100 °C. Bulb-to-bulb distillation of the crude product affords 10.0 g (98.9%) of enol phosphate **2a**: bp 85 °C (1.4 mmHg) [lit.[4,5] bp 133.5–134.5 °C (11 mmHg)]; IR (CCl_4) 1655 (C=C), 1280 and 1025 [$(EtO)_2PO$—O] 880 (C=CH_2) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 5.05 (t, 1, J = 2 Hz, C=CH_2), 4.57 (br s, 1, C=CH_2), 4.5–3.8 (m, 6, allylic-CH_2 and O$CH_2$$CH_3$), 1.07 (td, 6, J_1 = 7 Hz, J_2 = 2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 149.8 (d, J = 7.9 Hz, C=CO), 100.6 (d, J = 4.1 Hz, C=CH_2), 64.8 (d, J = 6.2 Hz, CH_2O), 43.4 (d, J = 6.6 Hz, CH_2Cl), 15.4 (d, J = 6.7 Hz, CH_3).

Diethyl 3-[(Diethoxyphosphoryl)oxy]isopropenyl Phosphate (3). A twofold excess of triethyl phosphite (26.5 g, 159 mmol) was added dropwise to 1,3-dichloropropane[4] (5.06 g, 39.8 mmol). Since addition of the first equivalent is exothermic, an ice bath was used to keep the temperature at 40 °C. After the addition was complete the reaction mixture was refluxed at 160 °C for 2 h; prolonged heating caused decomposition of the product. The excess triethyl phosphite was removed by bulb-to-bulb distillation (40 °C, 1 mmHg). The temperature was then raised (70 °C, 0.5 mmHg) to remove a small amount of 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (787 mg, 8%). Chromatography of the residue on silica gel using 100% EtOAc gave 11.4 g (86%) of the product as a clear oil: IR ($CHCl_3$) 2980 (CH, aliphatic), 1655 (C=C), 1275 (P=O), 1165 (P—O) 1030 (P—O) cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.35 (t, 12, J = 7 Hz, OCH_2CH_3), 2.80 (d, 2, J = 10 Hz, CH_2), 4.15 (m, 8, O$CH_2$$CH_3$), 4.80 and 5.10 (m, 2, C=CH_2). These IR data correspond to this product as reported in ref 5.

Allylic Bromination of 3. *N*-Bromosuccinimide (7.65 g, 43.0 mmol) in CCl_4 (35 mL) was added to phosphate **3** (11.4 g, 34.4 mmol) and a catalytic amount of azobis(isobutyronitrile) (30 mg). The reaction mixture was refluxed at 60 °C in the presence of a 200-W incandescent lamp for 24 h. Succinimide floats to the top of the mixture when the reaction is complete. After cooling to 23 °C, the succinimide was filtered from the reaction mixture and rinsed with CCl_4. The combined solvents were removed in vacuo. Chromatography on silica gel using 100% EtOAc gave 5.09 g (36%) of the product **2b** as a yellow oil: IR ($CHCl_3$) 2980 (CH, aliphatic), 1630 (C=C), 1275 (P=O), 1030 (P—O) cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.40 (t, 12, J = 7 Hz, OCH_2CH_3), 4.30 (m, 8, O$CH_2$$CH_3$), 4.65 (m, 2, CH_2), 5.85 (m, 1, C=CH).

Methyl (*Z*)-4-Bromo-3-[(diethoxyphosphoryl)oxy]-2-butenoate (2c). To a solution of enol phosphate 4[6] (2.00 g, 7.93 mmol) and freshly distilled CCl_4 (11.9 mL) were added *N*-bromosuccinimide (1.41 g, 7.93 mmol) and a catalytic amount of azobis(isobutyronitrile) (10 mg). The mixture was heated to reflux for 12 h with a 200-W incadescent lamp and then cooled and diluted with hexane (10 mL) and filtered. The filtrate was washed with saturated $NaHCO_3$ solution (3 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 200 g, 50% EtOAc in hexane as the eluant) to afford 1.75 g (67%) of bromide **2c**: bp 190 °C (0.05 mmHg); IR (CCl_4) 3050 (CH, vinylic), 2980 (CH, aliphatic), 1725 (C=O), 1640 (C=C), 1275 and 1030 [OP(OEt)$_2$] cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 6.00 (s, 1, C=CH), 4.61 (s, 2, C=CCH_2), 4.25 (m, 4, O$CH_2$$CH_3$), 3.74 (s, 3, $COOCH_3$), 1.40 (t, 6, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 164.7 (CO_2), 159.0 (d, J = 7.9 Hz, C=CO), 106.3 (d, J = 3.8 Hz, C=CCO_2), 64.6 (d, J = 6.2 Hz, CH_2O), 51.0 (CO_2CH_3), 24.8 (d, J = 6.8 Hz, CH_2Br), 15.3 (d, J = 6.6 Hz, CH_3).

Anal. Calcd for $C_9H_{16}BrO_6P$: C, 32.65; H, 4.87. Found: C, 32.70; H, 4.95.

Methyl 1-[2-[(Diethoxyphosphoryl)oxy]-2-propenyl]-2-oxocyclohexanecarboxylate (6a). An anhydrous mixture of THF (12 mL) and HMPA (3.0 mL) was added to washed potassium hydride (372 mg, 9.3 mmol) under N_2; the solution was stirred 5 min and then followed by the addition of 2-carbomethoxycyclohexanone (**5a**, 1.12 g, 0.96 mL, 7.2 mmol) dropwise at 23 °C. When the H_2 evolution ceased (~40 min), the reaction mixture was then cooled to 0 °C (ice bath) and charged with 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 1.80 g, 1.5 mL, 7.9 mmol). After the mixture was stirred at 0 °C for 5 min, the ice bath was removed, and the reaction mixture was allowed to stir at 23 °C for 35 h. The resulting solution was poured into a mixture of ice and saturated NaCl/H_2O (50 mL, 4:1) and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were washed with ice-cold H_2O (30 mL) and saturated NaCl/H_2O (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo to give 2.69 g of crude product. Column chromatography on silica gel (250 g) using absolute ether to elute the column gave 1.83 g (73%) of pure vinyl phosphate **6a**: bp 95 °C (0.08 mmHg); IR (CCl_4) 1730 and 1720 (C=O), 1660 (C=C), 1280 and 1025 [OPO(OEt)$_2$], 875 (C=CH_2) cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.33 [t, 6, J = 7 Hz, $(OCH_2CH_3)_2$], 1.50–3.03 (m, 10, -CH_2-), 3.70 (s, 3, CO_2CH_3), 4.07 [quintet, 4, J = 4 Hz, $(OCH_2CH_3)_2$], 4.43 and 4.83 (two br s, 2, C=CH_2).

Anal. Calcd for $C_{15}H_{25}O_7P$: C, 51.72; H, 7.23; P, 8.89. Found: C, 51.85; H, 7.27; P, 8.81.

Diethyl 1-[(2-Oxocyclohexyl)methyl]ethenyl Phosphate (6b). A few crystals of 2,2′-bipyridine, freshly distilled THF (3 mL), and freshly distilled diisopropylamine (0.154 mL, 1.1 mmol) were placed in a 15-mL, round-bottomed flask kept under a N_2

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atmosphere. The flask was cooled to −78 °C (dry ice/acetone bath) and *n*-butyllithium (1.55 M in hexane, 0.71 mL, 1.1 mmol) was added dropwise. After the reaction mixture was stirred for 15 min at −78 °C and 30 min at 0 °C, it was cooled again to −78 °C and cyclohexanone (**5b**, 0.10 mL, 1.0 mmol) was syringed dropwise into the flask. The reaction mixture was then allowed to warm up to 23 °C and stirring was continued for 30 min. Then, a solution of tetrakis(triphenylphosphine)palladium(0) (72 mg, 0.06 mmol) and 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 251 mg, 1.1 mmol) in freshly distilled THF (5 mL) was rapidly added. After being stirred for 15 min at 0 °C and 2 h at 23 °C, the reaction was quenched with saturated NH_4Cl solution (10 mL). The organic layer was separated and the aqueous layer was extracted with ether (5 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 40 g, using 60% EtOAc in hexane as eluant) affords 264 mg (91%) of compound **6b**: IR (CCl_4) 1725 (C=O), 1665 (C=C), 1275 and 1035 [$OPO(OEt)_2$] cm^{-1}; NMR (CCl_4, 60 MHz) δ 4.80 and 4.44 (two br s, 2, C=CH_2), 4.10 (quintet, 4, J = 7 Hz, OCH_2CH_3), 1.33 (t, 6, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_{13}H_{23}O_5P$: C, 53.79; H, 7.99; P, 10.67. Found: C, 53.94; H, 7.94; P, 10.36.

1-(1-Carbomethoxy-2-oxocyclohexyl)propan-2-one (7a). Methyl 1-[2-[(diethoxyphosphoyl)oxy]-2-propenyl]-2-oxocyclohexanecarboxylate (**6a**, 609 mg, 1.75 mmol) was dissolved in reagent-grade acetone (99.6%, 6 mL, J. T. Baker). The mixture was stirred for 5 min, hydrochloric acid (10%, 1 mL, 2.7 mmol) was then added, and the reaction mixture was heated to reflux for 3 h. The solution was allowed to cool to 23 °C. The solution was poured into mixture of saturated NaCl/H_2O and ice-cold H_2O (40 mL, 4:1) and extracted with Et_2O (5 × 30 mL). The combined ethereal extracts were washed with ice-cold H_2O (60 mL) and saturated NaCl/H_2O (2 × 60 mL), dried (Na_2SO_4), and concentrated in vacuo to give 372 mg of crude product. Column chromatography on silica gel (25 g), using a solution of 80% ether/20% petroleum ether to elute the column gave 0.342 g (92%) of product **7a**. Evaporative distillation gave colorless liquid diketo ester **7a**: bp 75 °C (0.16 mmHg) [lit.[2] bp 123–125 °C (0.05 mmHg)]; IR (CCl_4) 1740, 1725, and 1715 (C=O) cm^{-1}; NMR (CCl_4, 60 MHz) δ 2.10 (s, 3, CH_3CO), 2.73 (s, 2, -$COCH_2$-), 3.7 (s, 3, CO_2CH_3).

1-(2-Oxocyclohexyl)propan-2-one (7b). Diethyl 1-[(2-oxocyclohexyl)methyl]ethenyl phosphate (**6b**, 223 mg, 0.769 mmol) was dissolved in reagent-grade acetone (99.6%, 3.0 mL, J. T. Baker). The solution was stirred for 5 min and 10% HCl/H_2O (0.44 mL, 1.2 mmol) was then added. The reaction mixture was heated to reflux for 3 h. The solution was allowed to cool to 23 °C. The resulting solution was poured into NaCl/H_2O (15 mL) and extracted with Et_2O (3 × 30 mL). The combined etheral extracts were washed with H_2O (30 mL) and saturated NaCl/H_2O (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo to give 135 mg of crude product. Column chromatography on silica gel (10 g), using a solution 60% Et_2O/40% petroleum ether to elute the column gave 88.3 mg (84%) of product **7b**. Evaporative distillation gave colorless liquid diketone **7b**: bp 65 °C (0.23 mmHg) [lit.[2] bp 80 °C (0.2 mmHg) or bp 70 °C (0.1 mmHg)]; IR (CCl_4) 1725 and 1715 (C=O) cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.00–2.50 (m, 9), 2.10 (s, 3, CH_3CO), 2.90 (m, 2, -$COCH_2$-).

Methyl 2,3,4,5,6,7-Hexahydro-2-oxo-3a*H*-indene-3-carboxylate (8a). Anhydrous toluene (5.0 mL) was added to washed NaH (201 mg, 5.10 mmol) under N_2, and the mixture was heated to reflux. To this refluxing mixture was added over 2 h a solution of diketo ester **7a** in toluene (3.0 mL), and the resulting mixture was refluxed for 19 h. The solution was cooled to 0 °C (ice bath) and carefully acidified by adding slowly 10% HCl/H_2O, and the acidic solution was poured into ice-cold H_2O (15 mL) and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were washed with ice-cold H_2O (30 mL) and saturated NaCl/H_2O (2 × 30 mL), dried ($MgSO_4$), and concentrated in vacuo to give 210 mg of crude product. Column chromatography on silica gel (12 g), using a solution of 80% ether/20% petroleum ether to elute the column gave 180 mg (78%) of colorless liquid product **8a**. Evaporative distillation gave colorless product **8a**: bp 100 °C (0.15 mmHg) [lit.[2] bp 110 °C (0.05 mmHg)]; IR (CCl_4) 1750 and 1720 (C=O), 1625 (C=C) cm^{-1}; NMR (CCl_4, 60 mHz) δ 3.66 (s, 3, CO_2CH_3), 5.66 (s, 1, C=CH).

3,3a,4,5,6,7-Hexahydro-2(2*H*)-indenone (8b). Method A. 1-(1-Carbomethoxy-2-oxocyclohexyl)propan-2-one (**7a**, 124 mg, 0.585 mmol) was added to aqueous potassium hydroxide (5%, 8.5 mL, 6.4 mmol), and the mixture was heated to reflux for 6 h. The resulting mixture was allowed to cool to 23 °C and then poured into a mixture of 10% HCl/H_2O (60 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 0.0797 g of crude product. Column chromatography on silica gel (9 g), using a solution of 70% ether/30% petroleum ether to elute the column gave 0.0674 g (85%) of product **8b**. Evaporative distillation gave α,β-unsaturated ketone **8b**: bp 38 °C (0.23 mmHg) [lit.[2] bp 88 °C (4 mmHg)]; IR (CCl_4) 1710 (C=O), 1625 (C=C) cm^{-1}; NMR (CCl_4, 60 MHz), δ 0.90–3.00 (m, 9), 5.63 (s, 1, C=CH).

Method B. A 25-mL flask equipped with a condenser was charged with a few crystals of 2,2′-bipyridine, freshly distilled THF (3 mL), and freshly distilled diisopropylamine (0.15 mL, 1.1 mmol). The mixture was cooled to −78 °C (dry ice/acetone bath) and *n*-butyllithium (1.55 M in hexane, 0.71 mL, 1.1 mmol) was added dropwise. After the reaction mixture was stirred for 15 min at −78 °C and 30 min at 0 °C, it was cooled again to −78 °C and cyclohexanone (**5b**, 0.10 mL, 1.0 mmol) was added dropwise. The reaction mixture was then allowed to warm up to 0 °C, and after it was stirred for 30 min at this temperature a solution of tetrakis(triphenylphosphine)palladium(0) (66 mg, 0.06 mmol) and 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 251 mg, 1.1 mmol) in freshly distilled THF (5 mL) was added. After stirring for 15 min at 0 °C and 3 h at 23 °C, a mixture of 10% NaOH (8 mL) and ethanol (2 mL) was added. The resulting mixture was refluxed for 24 h and then cooled to 23 °C and extracted with Et_2O (5 × 10 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 30 g, 40% EtOAc in hexane as the eluant) affords 108 mg (79%) of product **8b**: bp 105 °C (5.5 mmHg) [lit.[2] bp 59–62 °C (0.05 mmHg)]; IR (CCl_4) 1710 (C=O), 1625 (C=C) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 5.80 (s, 1, C=CH), 3.25–0.75 (m, 11). These spectral data were comparable to those reported in the literature.[2]

Method C. Diethyl 1-[(2-oxocyclohexyl)methyl]ethenyl phosphate (**6b**, 0.260 g, 0.89 mmol) was added to aqueous potassium hydroxide (5%, 19 mL, 16.9 mmol). The mixture was heated to reflux for 8.5 h. The resulting solution was allowed to cool to 23 °C and the solution was poured into NaCl/H_2O (60 mL) and extracted with Et_2O (4 × 40 mL). The combined ethereal extracts were washed with H_2O (50 mL) and saturated NaCl/H_2O (50 mL), dried (Na_2SO_4), and concentrated in vacuo to give 110 mg of crude product. Column chromatography on silica gel (12 g) using a solution of 60% ether/40% petroleum ether to elute the column gave 100 mg (83%) of product **8b**. The IR and NMR spectra were identical with those obtained from the previous reactions.[2]

Desoxyallethrolone (11). Freshly distilled THF (20 mL) was added to washed NaH (625 mg, 260 mmol). To the rapidly stirring suspension of NaH/THF was added dropwise methyl acetoacetate (**9**, 2.33 g, 20.0 mmol). The reaction mixture was then stirred for 15 min and dry allyl bromide (2.94 g, 20.0 mmol, distilled from CaH_2, −40 mesh) was added all at once. After being stirred for 5 h at 23 °C, the reaction was quenched with 5% HCl (40 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Column chromatography of the crude product (silica gel 60, 340 g, 30 × 850 mm column, using 10% EtOAc in hexane as eluant) affords 2.8 g (90%) of compound **10a**: bp 70 °C (1.5 mmHg); IR (CCl_4) 3030 (C=CH_2), 1730 and 1710 (C=O), 1630 (C=C), 995 and 930 (CH=CH_2) cm^{-1}; NMR (CCl_4, 60 MHz) δ 6.1–5.4 (m, 1, CH=CH_2), 5.15–4.8 (m, 2, CH=CH_2), 3.7 (s, 3, CO_2CH_3), 3.4 (t, 1, J = 7 Hz, CH), 2.5 (br t, 2, J = 7 Hz, allylic-CH_2), 2.1 (s, 3, CH_3CO). This material was used immediately in the next step. To a vigorously stirring suspension of washed NaH (37 mg, 1.54 mmol) in freshly distilled THF (3 mL) was added dropwise β-keto ester **10a** (185 mg, 1.18 mmol). After the evolution of hydrogen had ceased the reaction mixture was cooled to 0 °C (ice/water bath) and *n*-butyllithium (1.55 M in hexane, 0.97 mL, 1.54 mmol) was rapidly syringed into the flask. An orange precipitate formed immediately and after this thick suspension was stirred vigorously for 5 min at 0 °C 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene

(**2a**, 352 mg, 1.54 mol) was added all in one portion. The reaction mixture was stirred for 10 min at 0 °C and 10 min at 23 °C; then a mixture of 100% EtOH (3.5 mL) and 10% NaOH (3.5 mL) was added and the resulting mixture was heated to 50 °C for 12 h. After being cooled to 23 °C the reaction mixture was extracted with Et_2O (5 × 5 mL). The ethereal extracts were combined, dried (Na_2SO_4), filtered, and concentrated to afford after chromatography (silica gel 60, 20 g, 10 × 300 mm column, 50% EtOAc in hexane as the eluent) 73 mg (46%) of desoxallethrolone (**11**): IR (CCl_4) 1700 (C=O), 990 and 910 (CH=CH_2) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 6.1–5.4 (m, 1, *CH*=CH_2), 5.1–4.7 (m, 2, CH=CH_2), 2.94 (d, 2, J = 5.9 Hz, allylic CH_2), 2.7–2.2 (m, 4, cyclic CH_2), 2.06 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 208.2 (CO), 170.8 (CH_3C=C), 137.7 (C=*C*C=O), 134.3 (*CH*=CH_2), 114.7 (CH=*CH*$_2$), 33.9 (CH_2), 31.3 (CH_2), 26.8 (CH_2), 16.8 (CH_3). The spectral data were identical with those reported in the literature.[13]

Methyl (*Z*)-2-[4-[(Diethoxyphosphoryl)oxy]-1-oxo-4-pentenyl]-4-heptenoate (13). *n*-Butyllithium (1.55 M in hexane, 0.68 mL, 1.05 mmol) was added at 0 °C to a 0.38 M solution of the sodium enolate anion of β-keto ester **12** in THF (2.5 mL), prepared from β-keto ester **12** (175 mg, 0.95 mmol) and washed NaH (30 mg, 1.25 mmol) according to the procedure described in the preparation of **11**. After the reaction mixture was stirred for 10 min at 0 °C, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 0.217 g, 0.95 mmol) was rapidly added and stirring was continued for 5 min at 0 °C and 10 min at 23 °C. The reaction was quenched with 10% HCl (4 mL) and the resulting mixture was extracted with Et_2O (3 × 5 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 30 g, 14 × 300 mm column, using 50% EtOAc in hexane as the eluant) to afford 271 mg (76%) of compound **13**: IR (CCl_4) 1745 and 1720 (C=O), 1660 (C=C), 1255 and 1015 [$OPO(OEt)_2$] cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 5.5–4.9 (m, 2, CH=CH), 4.7 and 4.4 (2 br s, 1, C=CH_2), 4.3–3.8 (quintet, 4, OCH_2CH_3), 3.65 (s, 3, $COOCH_3$), 3.4 (t, 1, J = 7 Hz, $CHCH_2$), 1.35 (t, 6, J = 7 Hz, OCH_2CH_3), 0.95 (t, 3, J = 7 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 202.95 (CO), 169.6 (CO_2), 153.9 (C=*C*O), 134.8 (*C*=C), 123.9 (C=*C*), 97.6 (C=*CH*$_2$), 64.25 (OCH_2), 58.5 ($COCHCO_2$), 52.3 (OCH_3), 39.1 (CH_2), 28.3 (CH_2), 25.9 (CH_2), 20.4 (CH_2), 15.96 (OCH_2CH_3), 13.97 (CH_3).

Anal. Calcd for $C_{17}H_{29}O_7P$: C, 54.25; H, 7.77. Found: C, 54.20; H, 7.80.

***cis*-Jasmone (14) via Base-Induced Cyclization of 13.** A mixture of enol phosphate **13** (56 mg, 0.148 mmol), 3% NaOH (2.4 mL), and THF (0.45 mL) was heated at 80 °C for 20 h. After it was cooled to 23 °C, the reaction mixture was acidified with 25% H_2SO_4 (0.5 mL) and extracted with Et_2O (5 × 1 mL). The combined ethereal extracts were washed with water (1 mL), dried (Na_2SO_4), and filtered. After the solvents were evaporated, the crude product was chromatographed (silica gel 60, 15 g, 8 × 300 mm column, using 50% EtOAc in hexane as the eluant) to give 22 mg (87%) of *cis*-jasmone (**14**): IR (CCl_4) 3015 (CH=CH), 1705 (C=O), 1650 (C=C), 890 (CH=CH) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 5.4–4.8 (m, 2, CH=CH), 2.95–2.70 (br d, 2, J = 5 Hz, CH_2CH=CH), 2.5–2.0 (m, 6, cyclic CH_2 and CH_2CH_3), 2.0 (s, 3, C=CCH_3), 0.95 (t, 3, J = 7 Hz $CHCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 208.9 (CO), 170.2 (CH_3C=C), 139.3 (C=*C*CO), 132.3 (*C*=C), 125.0 (C=*C*), 34.2 (CH_2), 31.6 (CH_2), 21.1 (CH_2), 20.5 (CH_2), 17.2 (CH_3), 14.1 (CH_3); mass spectrum, m/z (relative intensity) 164 (11.3), 91 (53), 79 (100), 77 (68), 67 (50), 55 (78), 41 (68), 39 (73). These spectral data were identical with those of an authentic sample of *cis*-jasmone.

From β-Keto Ester 12. β-Keto ester **12** (136 mg, 0.74 mmol) was added dropwise to a rapidly stirring suspension of washed sodium hydride (23 mg, 0.96 mmol). After the resulting clear solution was stirred for 30 min at 23 °C, it was cooled to 0 °C (ice/water bath) and *n*-butyllithium (1.55 M in hexane, 0.57 mL, 0.89 mmol) was rapidly syringed into the flask. The reaction mixture was stirred for 5 min at 0 °C and 15 min at 23 °C; then 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (1, 0.169 g, 0.74 mmol) was added all in one portion. After being stirred for 10 min at 0 °C and 1 h at 23 °C, the reaction was quenched with 20% NaOH (1.5 mL) and the resulting mixture was refluxed for 75 h. The reaction mixture was then allowed to cool to 23 °C; it was acidified with 25% H_2SO_4 and extracted with Et_2O (5 × 1 mL). The combined ethereal extracts were dried (Na_2SO_4) and concentrated. The crude product was chromatographed (silica gel 60, 80 g, 20 × 600 mm column, using 50% EtOAc in hexane as the eluant) to give 91 mg (75%) of *cis*-jasmone (**14**) which was identical with an authentic sample of *cis*-jasmone.

***tert*-Butyl Propionylacetate (17).**[19] The dione 2,2-dimethyl-1,3-dioxane-4,6-dione (**15**, 98%, 13.3 g, 106.1 mmol) was dissolved in freshly distilled CH_2Cl_2 (106 mL). This solution was cooled to 0 °C (ice/water bath) and freshly distilled pyridine (17.2 mL, 212.3 mmol) was added, followed by propionyl chloride (97%, 10.5 mL, 116.6 mmol). After the reaction mixture was stirred for 1 h at 0 °C and 1.5 h at 23 °C, it was washed with 5% HCl (100 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 × 20 mL). The organic extracts were combined, dried (Na_2SO_4), filtered, and concentrated in vacuo to give a crude oil. The ^1H NMR properties of this oil were consistent with the structure of the expected intermediate product: NMR ($CDCl_3$, 60 MHz) δ 15.0 (br s, 1, OH), 3.1 (q, 2, J = 7 Hz, CH_2CH_3), 1.7 [s, 9, $C(CH_3)_3$], 1.25 (t, 3, J = 7 Hz, CH_2CH_3). This crude oil was dissolved in benzene (100 mL) *tert*-butyl alcohol (30 mL, 318 mmol) was added, and the mixture was refluxed for 4 h and then concentrated in vacuo to give after bulb-to-bulb distillation 15.0 g (82%) of *tert*-butyl propionylacetate (**17**): bp 65 °C (5 mmHg); NMR ($CDCl_3$, 80 MHz) δ 3.30 (s, 2, CH_2COO-*t*-Bu), 2.50 (q, 2, J = 7.2 Hz, CH_2CH_3), 1.41 [s, 9, $C(CH_3)_3$], 1.02 (t, 3, J = 7.2 Hz, CH_2CH_3). This material was used immediately in the preparation of **18**, **23**, and **30**.

***tert*-Butyl Propionylacetate (17) from *tert*-Butyl Acetoacetate (16).**[16] *tert*-Butyl acetoacetate (**16**, 3.6 g, 22.7 mmol) was added dropwise to a suspension of washed NaH (575 mg, 23.9 mmol) in freshly distilled THF (55 mL). After it was stirred for 10 min, the clear solution was cooled to 0 °C (ice/water bath) and *n*-butyllithium (1.55 M in hexane, 16.1 mL, 25.9 mmol, Aldrich) was rapidly added. The reaction mixture was then stirred for 10 min at 0 °C and methyl iodide (1.57 mL, 25.9 mmol) was added in one portion. After being stirred for 5 min at 0 °C and 10 min at 23 °C, the reaction was quenched with 10% HCl (15 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed on silica gel (MPLC)[23] to afford 3.14 g (80%) of product **17**. This material was used immediately in the preparation of **18**, **23**, and **30**.

1,1-Dimethylethyl 4-[(Diethoxyphosphoryl)oxy]-2-(1-oxopropyl)-4-pentenoate (18). *tert*-Butyl propionylacetate (**17**, 5.25 g, 30.5 mmol) was added dropwise to a suspension of washed NaH (0.805 g, 33.5 mmol) in freshly distilled THF (30 mL). After the evolution of H_2 had ceased 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 7.65 g, 33.5 mmol) was added and the reaction mixture was heated to 60 °C for 7 h. The reaction was cooled to 23 °C and quenched with saturated NH_4Cl solution (50 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (MPLC,[23] 50% EtOAc in hexane) to afford 6.4 g (58%) of compound **18**: NMR ($CDCl_3$, 60 MHz) δ 4.85 and 4.53 (2 br s, 2, C=CH_2), 4.40–3.80 (m, 4, OCH_2CH_3), 3.72 (t, 1, J = 7 Hz, CH), 2.75–2.40 (m, 4, $CHCH_2$ and CH_3CH_2CO), 1.47 [s, 9, $C(CH_3)_3$], 1.36 (t, 6, J = 7 Hz, OCH_2CH_3), 1.07 (t, 3, J = 7 Hz, CH_3CH_2).

Anal. Calcd for $C_{16}H_{29}O_7P$: C, 52.74; H, 8.02. Found: C, 52.74; H, 7.99.

2,5-Heptanedione (19). The experimental procedure for preparing diketone **19** from compound **18** was the same as that described for the preparation of cyclopentenone **20** with the exception that 10% H_2SO_4 was used instead of 20% H_2SO_4. From compound **18** (4.9 g, 13.5 mmol) 1.5 g (88%) of diketone **19** was obtained: NMR ($CDCl_3$, 60 MHz) δ 2.75 (s, 4, CH_2CH_2), 2.5 (q, 2, J = 7.6 Hz, CH_3CH_2), 2.2 (s, 3, CH_3CO), 1.1 (t, 3, J = 7.6 Hz, CH_3CH_2). These spectral data were identical with those reported in the literature.[13,20]

2,3-Dimethylcyclopent-2-en-1-one (20, via Acid Hydrolysis of 18). Compound **18** (2.30 g, 6.33 mmol) was dissolved in 100% EtOH (22 mL) and 20% H_2SO_4 (10 mL). After the reaction mixture was refluxed for 3 days, it was cooled to 23 °C and extracted with Et_2O (3 × 10 mL). The combined extracts were

dried (Na_2SO_4) and filtered. The solvent were removed in vacuo and the resulting crude oil was chromatographed (silica gel 60, 80 g, 50% EtOAc in hexane as the eluant) to give 340 mg (48%) of cyclopentenone **20**: bp 80 °C (20 mmHg); IR (CCl_4) 1700 (C=O), 1650 (C=C) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.7–2.2 (m, 4, cyclic CH_2), 1.9 (s, 3, C=CCH_3), 1.7 (s, 3, C=CCH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 209.1 (CO), 169.4 (*C*=CCO), 135.6 (C=*C*CO), 33.6 (CH_2CO) 30.96 (CH_2), 16.6 (CH_3), 7.28 (CH_3). These spectral data were identical with those reported in the literature.[13,20]

Via Base-Induced Cyclization of 19. Diketone **19** (500 mg, 0.39 mmol) was added to 2% NaOH (6.4 mL) and 100% ethanol (1.8 mL). The reaction mixture was refluxed for 8 h; then it was allowed to cool to 23 °C and extracted with Et_2O (5 × 3 mL). The extracts were combined, dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 40 g, using 50% EtOAc in hexane as the eluant) affords 370 mg (86%) of cyclopentenone **20**.

Methyl [(Trimethylsilyl)methyl]propionylacetate. Methyl propionylacetate (2.32 g, 17.8 mmol) in freshly distilled dioxane (6 mL) was added dropwise to a stirred suspension of washed NaH (475 mg, 19.6 mmol) in dry HMPA (4.5 mL) and freshly distilled dioxane (6 mL). The reaction mixture was stirred at 23 °C until evolution of H_2 gas had ceased. The (iodomethyl)trimethylsilane (3.81 g, 17.8 mmol) in freshly distilled dioxane (7 mL) was added all in one portion. The resulting mixture was heated to reflux for 3 h; then the reaction was cooled to 23 °C and quenched with saturated NH_4Cl solution (20 mL). The resulting mixture was extracted with Et_2O (5 × 10 mL), and the combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo to give a crude oil which was chromatographed (silica gel 60, 300 g, 30 × 800 mm column, 50% EtOAc in hexane as the eluant) to afford after bulb-to-bulb distillation 3.16 g (83%) of β-keto ester: bp 70 °C (1.5 mmHg); IR (CCl_4) 1740 (C=O), 1725 (C=O), 1255 (CH_3Si) cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 3.49 (s, 3, CO_2CH_3), 3.24 (t, 1, J = 7 Hz, CH), 2.27 (q, 2, J = 7 Hz, CH_3CH_2), 0.93–0.74 (m, 5, CH_3CH_2 and $CH_2Si(CH_3)_3$), –0.20 [s, 9, $Si(CH_3)_3$].

Anal. Calcd for $C_{10}H_{20}O_3Si$: C, 55.52; H, 9.32. Found: C, 55.68; H, 9.00.

***tert*-Butyl [(Trimethylsilyl)methyl]propionylacetate (22).** Preparation of β-keto ester **22** was carried out according to the method described above for the preparation of the above methyl ester. From *tert*-butyl propionylacetate (**17**), 14.3 g, 83.2 mmol), 16.0 g (76%) of product **22** was obtained: bp 60 °C (0.9 mmHg); IR (CCl_4) 1740 and 1720 (C=O), 1255 ($SiCH_3$) cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 3.3 (t, 1, J = 7.6 Hz, CH), 2.6–2.3 (q, 2, J = 7 Hz, CH_3CH_2), 1.4 [s, 9, $C(CH_3)_2$], 1.1–0.8 (m, 5, $CH_2Si(CH_3)_3$), and CH_3CH_2).

Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.50; H, 10.09.

1,1-Dimethylethyl 4-[(Diethoxyphosphoryl)oxy]-2-(1-oxopropyl)-2-[(trimethylsilyl)methyl]-4-pentenoate (23). β-Keto ester **22** (14.5 g, 56.1 mmol) was added dropwise to a stirred suspension of washed NaH (1.61 g, 67.3 mmol) in THF (56 mL). After the evolution of H_2 had ceased, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 14.1 g, 61.7 mmol) was added and the resulting mixture was heated to 60 °C for 4 h. The reaction was cooled to 23 °C and quenched with 5% H_2SO_4 (100 mL) and the resulting mixture was extracted with Et_2O (5 × 30 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Removal of the volatile compounds contained in the crude product by bulb-to-bulb distillation (100 °C/1.5 mmHg) affords 25.3 g (85%) of product **23**: NMR ($CDCl_3$, 80 MHz) δ 4.67 and 4.20 (2 t, 2, J = 1 Hz, C=CH_2), 4.05–3.65 (m, 4, OCH_2CH_3), 2.55 (s, 2, allylic-CH_2), 2.28 (q, 2, J = 7.3 Hz, CH_3CH_2CO), 1.25 [s, 9, $C(CH_3)_3$], 1.15 (t, 6, J = 7 Hz, OCH_2CH_3), 0.85 (t, 3, J = 7.3 Hz, CH_3CH_2CO), –0.12 [s, 9, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 206.5 (CO), 170.7 (CO_2), 151.1 (C=CO), 98.95 (C=CH_2), 81.15 (CO), 63.3 (CO), 60.4 (CH_2O), 39.8 (C=C(O)CH_2, 30.7 (CH_3CH_2), 26.96 [$(CH_3)_3$], 19.4 (CH_3), 15.2 (CH_3CH_2O), 7.18 (CH_2Si), –0.57 (CH_3Si). An analytical sample of **23** was obtained by chromatography on silica gel using 75% EtOAc in hexane as the eluant.

Anal. Calcd for $C_{20}H_{39}O_7PSi$: C, 53.31; H, 8.72. Found: C, 53.22; H, 8.70.

2,3-Dimethyl-5-[(trimethylsilyl)methyl]cyclopent-2-en-1-one (24, from β-Keto Ester 22). To washed NaH (286 mg, 10.4 mmol) was added freshly distilled THF (10 mL). β-Keto ester **22** (2.44 g, 9.44 mmol) was added dropwise under vigorous stirring. After evolution of H_2 had ceased (ca. 15 min), 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 2.16 g, 9.44 mmol) was rapidly added and the mixture was heated to 65 °C for 5 h. A mixture of 100% ethanol (53 mL) and 2% NaOH (190 mL) was added and the reaction mixture was refluxed for 5 days. After it was cooled to 23 °C, the reaction mixture was extracted with Et_2O (5 × 50 mL) and the combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 200 g, 50% EtOAc in hexane as the eluant) affords 734 mg (40%) of cyclopentenone **24**: bp 55 °C (1 mmHg); IR (neat) 1700 (C=O), 1655 (C=C), 1250 (CH_3Si) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.8–1.9 (m, 3, cyclic H), 2.01 (s, 3, C=CCH_3), 1.68 (s, 3, CH_3C=C), 1.05 (dd, 1, J_{AB} = 14.5 Hz, J_{BC} = 4 Hz, $CH_aSi(CH_3)_3$), 0.25 (dd, 1, J_{AB} = 14.5 Hz, J_{AC} = 12 Hz, $CH_bSi(CH_3)_3$), –0.1 [s,9, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 212.5 (CO), 167.2 (*C*=CCO), 134.8 (C=*C*CO), 41.1 (CH, CH_2), 19.0 (CH_3C=C), 16.9 (C=CCH_3), 7.98 (CH_2Si), –0.99 [$(CH_3)_3Si$]; mass spectrum (70 eV), m/z (relative intensity) 196 (M^+, 41), 181 (100), 75 (68), 73 (79).

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 66.93; H, 10.09.

Via Base-Induced Cyclization of 23. After a mixture of enol phosphate **23** (558 mg, 1.24 mmol), 2% NaOH (24 mL), and 100% ethanol (7 mL) was refluxed for 4 days, it was extracted with Et_2O (5 × 10 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 30 g, using 50% EtOAc as the eluant) to afford 150 mg (62%) of cyclopentenone **24**.

Methylenomycin B (21). To a solution of 2,3-dimethyl-5-[(trimethylsilyl)methyl]cyclopent-2-en-1-one (**24**, 302 mg, 1.54 mmol) in CCl_4 (3 mL) was added a solution of Br_2 (0.66 M in CCl_4, 4.7 mL, 3.08 mmol). After the reaction mixture was stirred for 10 h at 23 °C, 5% $NaHCO_3$ (6 mL) was added and the mixture was extracted with Et_2O (5 × 5 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 30 g, 20% EtOAc in hexane as the eluant) affords 308 mg of a dibromo product. A 80-MHz ^1H NMR spectrum indicated the absence of the $Si(CH_3)_3$ group in this product. Low-resolution mass spectroscopy showed a molecular ion M^+ 282 and a peak pattern typical of a dibromo compound. This product was used directly in the next step without further purification. A 25-mL flask kept under a N_2 atmosphere was charged with powdered Zn (154 mg, 2.43 mmol), freshly distilled ether (5.4 mL), and acetic acid (134 μL). The flask was cooled to 0 °C (ice/water bath) and a solution of the bromination product (308 mg) in freshly distilled Et_2O (2.7 mL) was added dropwise. The reaction mixture was stirred for 10 min at 10 °C and 30 min at 23 °C. After pyridine (0.3 mL) was added, a white precipitate formed which was filtered. The Et_2O layer was washed with H_2O (2 × 5 mL) and 5% Na_2CO_3 (5 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo to give 135 mg (64% overall yield) of methylenomycin B (**21**): NMR ($CDCl_3$, 80 MHz) δ 6.03 (s, 1, C=CH), 5.33 (s, 1, C=CH), 3.09 (s, 2, CH_2), 2.09 (s, 3, CH_3), 1.78 (s, 3, CH_3). These NMR data were identical with those reported in the literature.[18]

Methyl α-[(Trimethylsilyl)methyl]acetoacetate (25). Methyl acetoacetate (**9**, 1.20 g, 10.3 mmol) in freshly distilled dioxane (3 mL) was added dropwise to a stirred suspension of washed NaH (296 mg, 12.3 mmol) in dry HMPA (2.6 mL) and freshly distilled dioxane (3 mL). After evolution of H_2 ceased, (iodomethyl)trimethylsilane (2.20 g, 10.3 mmol) in freshly distilled dioxane (4 mL) was added all in one portion. After the reaction mixture was heated to reflux for 3 h, the reaction was cooled to 23 °C and quenched with saturated NH_4Cl solution (40 mL). The mixture was extracted with Et_2O (3 × 30 mL), and the combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 200 g, 50% EtOAc in hexane as the eluant) to afford after bulb-to-bulb distillation 1.56 g (75%) of β-keto ester **25**: bp 60 °C (2 mmHg); IR (CCl_4) 2950 (CH, aliphatic), 1740 (C=O), 1720 (C=O), 1250 (CH_3Si) cm^{-1}; NMR ($CDCl_4$, 80 MHz) δ 3.50 (s, 3, CO_2CH_3), 3.25 (t, 1, J = 6.3 Hz, CH), 1.99 (s, 3, CH_3CO), 0.88 (d,

2, J = 6.3 Hz, CH_2), −0.20 [s, 9, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 202.5 (CO), 170.5 (CO_2), 54.75 (OCH_3), 51.5 ($COCH-CO_2$), 27.0 (CH_3CO), 14.6 (CH_2Si), −2.20 [$(CH_3)_3Si$].

Anal. Calcd for $C_9H_{18}O_3Si$: C, 53.43; H, 8.97. Found: C, 53.31; H, 8.80.

Methyl γ-[(Trimethylsilyl)methyl]acetoacetate (27). To a washed NaH (190 mg, 7.8 mmol) was added freshly distilled THF (12 mL) followed by dropwise addition of methyl acetoacetate (**9**, 697 mg, 6.0 mmol). After the resulting solution was stirred for 15 min, it was cooled to 0 °C (ice/water bath) and *n*-butyllithium (1.55 M in hexane, 4.65 mL, 7.2 mmol) was rapidly added. The reaction mixture was stirred for 10 min at 0 °C and (iodomethyl)trimethylsilane (1.41 g, 6.60 mmol) was added all in one portion. The mixture was then allowed to warm to 23 °C and after stirring for 30 min, the reaction was quenched with 5% H_2SO_4 (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 80 g, 20 × 600 mm column, using 50% EtOAc in hexane as the eluant) afford 900 mg (74%) of product **27**: bp 50 °C (1.5 mmHg); NMR ($CDCl_3$, 80 MHz) δ 3.45 (s, 3, CO_2CH_3), 3.23 (s, 2, $CH_2CO_2CH_3$), 2.28 (t, 2, J = 8.1 Hz, CH_2CH_2CO), 0.52 (t, 2, J = 8.1 Hz, $CH_2Si(CH_3)_3$), −0.05 [s, 9, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 202.6 (CO), 167.1 (CO_2), 51.3 (OCH_3), 47.6 ($COCH_2CO_2$), 36.9 (CH_2CO), 9.28 (CH_2Si), −2.53 [$(CH_3)_3Si$].

Anal. Calcd for $C_9H_{18}O_3Si$: C, 53.43; H, 8.97. Found: C, 53.27; H, 8.75.

2-[(Trimethylsilyl)methyl]-3-methylcyclopent-2-en-1-one (26, from β-Keto Ester 27). To a suspension of washed NaH (36 mg, 1.5 mmol) in freshly distilled THF (2.5 mL) was added dropwise β-keto ester **27** (250 mg, 1.23 mmol). After the evolution of H_2 ceased 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 280 mg, 1.23 mmol) was rapidly added. The reaction mixture was heated to 65 °C for 4 h; then 10% NaOH (5 mL) was added and the reaction mixture was refluxed for 15 h. After it was cooled to 23 °C, the mixture was extracted with Et_2O (5 × 3 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 30 g, using 50% EtOAc in hexane as the eluant) afforded 72 mg (30%) of crystalline cyclopentenone **26**: mp 56–57 °C [lit.[22] mp 58–58.5 °C]; bp 45 °C (0.6 mmHg) [lit.[22] bp 118 °C (21 mmHg)]; IR ($CDCl_3$) 1700 (C=O), 1630 (C=C), 1200 (CH_3Si) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.6–2.2 (m, 4, cyclic CH_2), 1.95 (s, 3, $C=CCH_3$), 1.6 (s, 2, $CH_2Si(CH_3)_3$), −0.05 [s, 9, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 165.3 (C=CCO), 138.4 (C=CCO), 33.90 (CH_2CO), 31.15 ($CH_2C=C$), 17.48 (CH_3), 13.09 (CH_2Si), −1.30 [$(CH_3)_3Si$].

Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.65; H, 10.11.

From β-Keto Ester 25. To a 0.33 M solution of the enolate anion of β-keto ester **25** in THF at 0 °C, prepared from β-keto ester **25** (100 mg, 0.47 mmol) and washed NaH (15 mg, 0.61 mmol) in THF (1.5 mL), was added *n*-butyllithium (1.55 M in hexane, 0.34 mL, 0.52 mmol). After the mixture was stirred for 10 min at 0 °C, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 119 mg, 0.52 mmol) was rapidly added. The reaction mixture was stirred for 10 min at 0 °C and 10 min at 23 °C; then 2% NaOH (5.6 mL) was added and stirring was continued for 3 days at 23 °C. The mixture was extracted with Et_2O (5 × 3 mL) and the combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 10 g, using 50% EtOAc in hexane as eluant) to afford 25 mg (29%) of cyclopentenone **26**.

Via Acid Hydrolysis of 30. The experimental procedure for the preparation of cyclopentenone **27** from compound **30** was the same as that used to prepare cyclopentanone **20** from compound **18**. From phosphate **30** (500 mg, 1.10 mmol), 185 mg (86%) of pure crystalline cyclopentenone **26** was isolated.

Via Base-Induced Cyclization of 31. The same procedure as that employed for the preparation of cyclopentenone **20** from diketone **19** was used. From 824 mg (4.12 mmol) of dione **31**, 683 mg (86%) of cyclopentenone **26** was obtained.

***tert*-Butyl γ-[(Trimethylsilyl)methyl]acetoacetate (29).** The experimental procedure for the preparation of compound **29** was the same as that used for the preparation of **27**. From 1.41 g (9.1 mmol) of *tert*-butyl acetoacetate (**16**), 2.07 g (93%) of product **29** was produced: bp 55 °C (1.2 mmHg); IR (CCl_4) 1740 and 1720 (C=O), 1250 (CH_3Si) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 3.22 (s, 2, CH_2COO-*t*-Bu), 2.45 (t, 2, J = 7.3 Hz, CH_2CH_2CO), 1.34 [s, 9, $C(CH_3)_3$], 0.77 (t, 2, J = 7.3 Hz, CH_2Si), −0.11 [s, 9, $(CH_3)_3Si$]; ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 203.2 (CO), 166.0 (CO_2), 81.0 (CO), 49.5 ($COCH_2CO_2$), 36.7 (CH_2CO), 27.5 (CH_3), 9.49 (CH_2Si), −2.37 [$(CH_3)_3Si$].

Anal. Calcd for $C_{12}H_{24}O_3Si$: C, 58.97; H, 9.90. Found: C, 58.97; H, 9.72.

1,1-Dimethylethyl 4-[(Diethoxyphosphoryl)oxy]-2-[1-oxo-3-(trimethylsilyl)propyl]-4-pentenoate (30). To washed NaH (115 mg, 2.92 mmol) was added freshly distilled THF (5 mL). The mixture was vigorously stirred and β-keto ester **29** (595 mg, 2.43 mmol) was added dropwise. After the clear solution was stirred for 15 min, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 6.11 g, 2.67 mmol) was rapidly added and the reaction mixture was heated to 70 °C for 7 h. The reaction was cooled to 23 °C and then quenched with saturated NH_4Cl solution (5 mL), the organic layer was separated, and the aqueous layer was extracted with ether (5 × 2 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 80 g, using 50% EtOAc in hexane as the eluant) affords 850 mg (80%) of enol phosphate **30**: IR (CCl_4) 1740 and 1720 (C=O), 1670 (C=C), 1250 (CH_3Si), 1275 and 1015 [$OPO(OEt)_2$] cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 4.8 (t, 1, J = 1 Hz, C=CH), 4.4 (t, 1, J = 1 Hz, C=CH), 4.4–3.7 (m, 4, OCH_2CH_3), 3.6 (t, 1, J = 7.4 Hz, CH), 2.7–2.3 (m, 4, CH_2CO and $CHCH_2$), 1.4 [s, 9, $C(CH_3)_3$], 1.2 (t, 6, J = 7 Hz, OCH_2CH_3), 0.8–0.4 (m, 2, $CH_2Si(CH_3)_3$), −0.1 [s, 9, $Si(CH_3)_3$].

Anal. Calcd for $C_{19}H_{37}O_7PSi$: C, 52.27; H, 8.54. Found: C, 52.29; H, 8.46.

8,8-Dimethyl-8-silanonane-2,5-dione (31) Method A. Enol phosphate **30** (850 mg, 1.95 mmol) was added to 10% H_2SO_4 (7 mL) and 100% ethanol (3 mL). After the mixture was refluxed for 4 days, it was cooled to 23 °C and extracted with Et_2O (3 × 5 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 20 g, 50% EtOAc in hexane as the eluant) to afford 373 mg (96%) of dione **31**: NMR ($CDCl_3$, 60 MHz) δ 2.6 (br s, 4, CH_2CH_2), 2.5–2.1 (m, 2, $CH_2CH_2Si(CH_3)_3$), 2.1 (s, 3, CH_3CO), 0.8–0.5 (m, 2, $CH_2CH_2Si(CH_3)_3$), −0.1 [s, 9, $Si(CH_3)_3$].

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.75; H, 9.96.

Method B. This procedure was the same as that used to prepare cyclopentenone **26** from compound **30** with the exception that reagent-grade acetone instead of absolute ethanol was used as cosolvent at 17-h reflux. From enol phosphate **30** (2.0 g, 4.5 mmol), 0.91 g (100%) of dione **31** was obtained.

Methyl (*Z*)-1-[2-[(Diethoxyphosphoryl)oxy]-4-methoxy-4-oxo-2-butenyl]-2-oxocyclohexanecarboxylate (Entry 4). To a stirred suspension of washed NaH (76 mg, 3.15 mmol) in freshly distilled THF (9.2 mL) was added dropwise 2-carbomethoxycyclohexanone (411 mg, 2.64 mmol). After 10 min, the evolution of H_2 ceased and (*Z*)-methyl 4-bromo-[(diethoxyphosphoryl)oxy]-2-butenoate (**2c**, 874 mg, 2.64 mmol) was added all at once. After stirring for 4 h at 23 °C, a saturated NH_4Cl solution (10 mL) and water (3 mL) were added. The organic layer was separated and the aqueous layer was extracted with Et_2O (5 × 3 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Chromatography of the crude product (silica gel 60, 40 g, 50% EtOAc in hexane as the eluant) gives 965 mg (90%) of product (entry 4): NMR ($CDCl_3$, 80 MHz) δ 5.97 (s, 1, C=CH), 4.4–3.8 (m, 4, OCH_2CH_3), 3.75 (s, 3, CO_2CH_3) 3.70 (s, 3, CO_2CH_3), 2.7–2.2 (br m, 4, CH_2CO and $C=CCH_2$), 2.35 (t, 6, J = 7.6 Hz, OCH_2CH_3); ^{13}C NMR ppm 204.8 (CO), 170.6 (CO_2), 165.8 (CO_2), 161.9 (C=CO), 106.7 (C=CH), 64.4 (OCH_2), 59.0 (CCO), 52.0 (CH_3O), 50.8 (CH_3O), 40.2 (CH_2CO), 35.4 ($C=CCH_2$), 34.35 (CH_2), 26.8 (CH_2), 21.8 (CH_2), 15.5 (CH_3).

Anal. Calcd for $C_{17}H_{27}O_9P$; C, 50.25; H, 6.70. Found: C, 50.20; H, 6.81.

Methyl 1-[2-[(Diethoxyphosphoryl)oxy]-2-propenyl]-4,4-dimethyl-2-oxocyclopentanecarboxylate (Entry 10). To a rapidly stirring suspension of washed NaH (560 mg, 2.19 mmol) in THF (2 mL) was added dropwise 2-(methoxycarbonyl)-4,4-

dimethylcyclopentanone (338 mg, 1.10 mmol). After the enolate anion was allowed to form for 5 h at 23 °C, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 454 mg, 1.19 mmol) was added. The reaction mixture was stirred for 17 h at 60 °C and then cooled to 23 °C and quenched with saturated NH_4Cl solution (30 mL) and extracted with Et_2O (4 × 10 mL). The ethereal extracts were combined, dried (Na_2SO_4), filtered, and concentrated in vacuo to give 564 mg of crude oil. Chromatography of this crude oil (silica gel 60, 80 g, 15 × 800 mm column, using 80% ether in petroleum ether as eluant) affords 433 mg (60%) of product (entry 10): IR (CCl_4) 2925 (CH, aliphatic) 1755 (C=O), 1725 (C=O), 1655 (C=C), 1275 and 1030 [OPO(OEt)$_2$] cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 4.92 (t, 1, J = 2 Hz, C=CH), 4.55 (br s, 1, C=CH), 4.40–3.85 (m, 4, OCH_2CH_3), 3.6 (s, 3, CO_2CH_3), 1.37 (t, 6, J = 7.6 Hz, OCH_2CH_3), 1.12 (br s, 6, CH_3).

Anal. Calcd for $C_{16}H_{27}O_7P$: C, 53.03; H, 7.51. Found: C, 52.90; H, 7.30.

Methyl 4,4-Dimethyl-2-oxo-1-(2-oxopropyl)cyclopentanecarboxylate. The above enol phosphate (226 mg, 0.625 mmol) was dissolved in reagent-grade acetone (4.5 mL) and 10% HCl (0.5 mL). The reaction mixture was refluxed for 9.5 h with stirring; then it was cooled to 23 °C, diluted with H_2O (20 mL), and extracted with Et_2O (3 × 10 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated to afford 94 mg of crude oil. Column chromatography (silica gel 60; 20 g, 10 × 300 mm, column using 80% ether in petroleum ether as eluant) gives 92 mg (65%) of product: IR (CCl_4) 1740 and 1720 (C=O) cm^{-1}; NMR (CCl_4, 60 MHz) δ 3.6 (s, 3, CO_2CH_3), 2.3 (s, 2, CH_2COCH_3), 2.1 (s, 3, $COCH_3$), 1.2 (s, 3, CH_3), 1.1 (s, 3, CH_3).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.82, H, 8.10.

Methyl 1-[2-[(Diethoxyphosphoryl)oxy]-2-propenyl]-2-oxocyclopentanecarboxylate (Entry 11). To washed NaH (868 mg, 36.2 mmol) was added freshly distilled THF (24 mL). 2-Carbomethoxycyclopentanone (3.43 g, 24.1 mmol) was then added dropwise with rapid stirring. After the reaction mixture was stirred for 1.5 h at 23 °C, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 5.51 g, 24.1 mmol) was rapidly added and the reaction mixture was heated to 60 °C for 23 h. The reaction was cooled to 23 °C and then quenched with saturated NH_4Cl solution (150 mL) and extracted with Et_2O (4 × 50 mL). The combined ethereal extracts were dried (Na_2SO_4) and concentrated in vacuo to give 6.6 g of crude oil. This material was chromatographed (silica gel 60, 70% EtOAc in hexane as the eluant) to afford 6.1 g (76%) of product (entry 11): bp 115 °C (0.7 mmHg); IR (CCl_4) 1760 (C=O), 1730 (C=O), 1650 (C=C), 1275 and 1020 [OPO(OEt)$_2$] cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 4.92 (t, 1, J = 2 Hz, C=CH), 4.55 (t, 1, J = 2 Hz, C=CH), 4.40–3.85 (m, 4, OCH_2CH_3), 3.67 (s, 3, CO_2CH_3), 1.35 (t, 6, J = 7.6 Hz, OCH_2CH_3); ^{13}C NMR ppm 212.9 (CO), 170.2 (CO_2), 151.1 (C=CO), 99.7 (C=CH_2), 63.9 (CH_2O), 58.4 (CH_3O), 52.2 (CH_3), 40.1 (CH_2C=C), 37.2 (CH_2), 31.2 (CH_2), 19.1 (CH_2).

Anal. Calcd for $C_{14}H_{23}O_7P$: C, 50.30; H, 6.93. Found: C, 49.69; H, 7.14.

Methyl 2-Oxo-1-(2-oxopropyl)cyclopentanecarboxylate. The above enol phosphate (404 mg, 1.20 mmol) was dissolved in 95% EtOH (4.2 mL). To this solution was added 20% H_2SO_4 (2 mL). After the reaction mixture was heated at reflux for 21 h, it was cooled to 23 °C, diluted with water (15 mL), and extracted with ether (4 × 30 mL). The combined ether extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo to give 0.282 g of crude oil. Column chromatography (silica gel 60, 20 g, using 70% ethyl acetate in hexane as the eluant) affords 112 mg (96%) of product: IR (CCl_4), 1740, and 1720 (C=O) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 3.69 (s, 3, CO_2CH_3), 3.05 (AB, 2, J_{AB} = 18 Hz, CH_2COCH_3), 2.13 (s, 5, CH_2COCH_3); ^{13}C NMR (20.2 MHz, $CDCl_3$) ppm 214.0 (CO), 204.8 (CO), 170.7 (CO_2), 57.2 (CH_3O), 52.3 ($COCCO_2$), 47.3 (CH_2CO), 37.3 (CH_2CO), 32.9 (CH_3CO), 29.6 (CH_2), 19.5 (CH_2).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.64; H, 7.14.

Methyl 2-Acetyl-4-[(diethoxyphosphoryl)oxy]-4-pentenoate (Entry 12). To washed NaH (226 mg, 5.74 mmol) was added anhydrous THF (5 mL) followed by methyl acetoacetate (555 mg, 4.78 mmol) with stirring under N_2. After stirring at 25 °C for 1 h, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 1.09 g, 4.78 mmol) was added. The resulting reaction mixture was stirred at 25 °C for 3 h and then at 60 °C for 6 h. After being cooled to 25 °C, the reaction was quenched with saturated NH_4Cl solution (30 mL) and the mixture extracted with Et_2O (3 × 20 mL). The combined ethereal extracts were washed with saturated NaCl solution, dried (Na_2SO_4), filtered (Na_2SO_4), and concentrated in vacuo to give 1.39 g of crude product. Chromatography on silica gel 60 (40 g) using 70% EtOAc in hexane afforded 0.973 g (67%) of product (entry 12): bp 160 °C (0.5 mmHg); NMR (80 MHz, $CDCl_3$) δ 1.36 (t, 6 H, J = 7.1 Hz, OCH_2CH_3), 2.28 (s, 3, CH_3CO), 2.76 (d, 2, J = 7.2 Hz, CH_2), 3.75 (s, 3, CO_2CH_3), 4.15 (m, 4, OCH_2CH_3), 4.58 and 4.89 (2 br s, 2, CH_2=C); ^{13}C NMR (20.2 MHz, $CDCl_3$) ppm 15.7 (CH_3CH_2), 29.2 (CH_3CO), 32.8 (CH_2), 52.2 (OCH_3), 56.2 (CH), 64.2 (OCH_2), 98.9 (CH_2=C), 151.6 (=CODEP), 168.8 (CO_2), 203 (CO).

Anal. Calcd for $C_{12}H_{21}O_7P$: C, 46.76; H, 6.87. Found: C, 46.63; H, 6.81.

***tert*-Butyl 2-Acetyl-4-[(diethoxyphosphoryl)oxy]-4-pentenoate (Entry 13).** This compound was prepared by a procedure analogous to that used for the above ester (entry 12). From *tert*-butyl propionylacetate (**17**, 5.25 g, 30.5 mmol) and **2a** (7.65 g, 229 mmol) was produced 6.4 g (58%) of product (entry 13): NMR (80 MHz, $CDCl_3$) δ 1.06 (t, 3, J = 7.6 Hz, CH_3), 1.36 (t, 3, J = 7.6 Hz, CH_3), 1.47 (s, 9, *t*-Bu), 2.3–2.85 (m, 4, CH_2C=C, CH_2CO), 4.15 (m, 4, OCH_2), 4.53 and 4.85 (two br s, 2, C=CH_2).

Anal. Calcd for $C_{16}H_{29}O_7P$: C, 52.74; H, 8.02. Found: C, 52.74; H, 7.99.

Dimethyl 4-Hydroxy-2-methyl-1,3-cyclopentadiene-1,3-dicarboxylate (Entry 14). Methyl acetoacetate (177 mg, 1.52 mmol) was added dropwise to a suspension of washed NaH (39 mg, 1.62 mmol) in freshly distilled THF (8 mL). After the evolution of H_2 ceased, (*Z*)-methyl 4-bromo-3-(diethoxyphosphoryl)oxy]-2-butenoate (**2c**, 0.503 g, 1.52 mmol) was added and the mixture was stirred for 20 h at 23 °C. The reaction was quenched with saturated NH_4Cl solution (5 mL), the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 3 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was chromatographed (silica gel 60, 60 g, 14 × 600 mm column, using 50% EtOAc in hexane as eluant) to give 210 mg (65%) of product (entry 14): NMR ($CDCl_3$, 80 MHz) δ 6.46 (s, 1, OH), 3.79 (s, 3, CO_2CH_3), 3.72 (s, 3, CO_2CH_3), 3.62 (s, 2, CH_2), 2.54 (s, 3, CH_3); ^{13}C NMR (20.2 MHz, $CDCl_3$) ppm 169.1 (CO_2), 164.1 (CO_2), 158.7 (C=COH), 145.6 (HOC=CCO_2), 114.0 (C=CCO_2), 108.8 (C=CMe), 52.0 (CH_3O), 51.0 (CH_3O), 33.4 (CH_2), 13.4 (CH_3); mass spectrum (70 eV), m/z (relative intensity) 212 (M^+, 26), 181 (22), 153 (100), 121 (63).

Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.48; H, 5.61.

1,1-Dimethylethyl 4-[(Diethoxyphosphoryl)oxy]-4-pentenoate (Entry 15). A 15-mL, round-bottomed flask equipped with a N_2 inlet and a magnetic stirring bar was charged with freshly distilled THF (1 mL) and freshly distilled diisopropylamine (0.30 mL, 2.14 mmol). This solution was cooled to −78 °C (dry ice/acetone bath) and *n*-butyllithium (1.55 M in hexane, 1.38 mL, 2.14 mmol) was added dropwise. After the reaction mixture was stirred for 15 min at −78 °C and 15 min at 0 °C, it was cooled again to −78 °C and *tert*-butyl acetate (**16**, 0.28 mL, 2.08 mmol) was syringed into the flask dropwise. The solution of the enolate anion was stirred for 30 min at −78 °C; then a solution of 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 476 mg, 2.08 mmol) and tetrakis(triphenylphosphine)palladium(0) (104 mg, 0.09 mmol) in freshly distilled THF (5 mL) was rapidly added. After the reaction mixture was stirred for 15 min at −78 °C, 15 min at 0 °C, and 20 h at 23 °C, the reaction was quenched with saturated NaCl solution (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (5 × 3 mL). The organic extracts were combined, dried (Na_2SO_4), filtered, and concentrated in vacuo. Column chromatography of the crude product (silica gel 60, 80 g, using 30% EtOAc in hexane as eluant) gave 362 mg (56.5%) of product (entry 15): IR (CCl_4) 1725 (C=O), 1655 (C=C), 1275 and 1000 [OPO(OEt)$_2$] cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 4.86 and 4.54 (2 br s, 2, C=CH_2), 4.35–3.90 (m, 4, OCH_2CH_3), 2.46 (s, 4, CH_2CH_2), 1.44 [s, 9, $C(CH_3)_3$], 1.36 (t, 6, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 171.1 (CO_2), 153.9 (C=CO), 97.0 (C=CH_2), 80.2 (CO), 64.0 (CH_2O), 32.2

(CH_2CO), 29.7 ($CH_2C{=}C$), 27.7 [$(CH_3)_3$], 15.7 (CH_3CH_2).

Anal. Calcd for $C_{13}H_{25}O_6P$: C, 50.64; H, 8.17. Found: C, 50.11; H, 7.94.

Cyclohexylidenemethyl Diethyl Phosphate (Entries 16–19). Method A. To washed KH (120 mg, 3.0 mmol) was added distilled THF (6 mL). The mixture was vigorously stirred and cyclohexanecarboxaldehyde (257 mg, 2.3 mL) in freshly distilled THF (1 mL) was added dropwise. After the reaction mixture as stirred for 15 min at 23 °C, 3-chloro-2-[(diethoxyphosphoryl)-oxy]-1-propene (**2a**, 525 mg, 2.3 mmol) in freshly distilled THF (1 mL) was syringed into the flask. After the reaction mixture was stirred for 1 h, saturated NH_4Cl solution (2 mL) was added and the resulting mixture was extracted with Et_2O (5 × 2 mL). The combined ethereal extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo to give a crude oil which was chromatographed (silica gel 60, 80 g, 50% EtOAc in hexane as the eluant) to afford 365 mg (64%) of product (entry 16): bp 85 °C (1.1 mmHg); IR (CCl_4) 1275 and 1035 [$PO(OEt)_2$], 1680 (C=C) cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 6.22 (m, 1, C=CH), 4.14 (m, 4, OCH_2CH_3), 2.22 and 1.98 (2 br s, 4, allylic-H), 1.34 (t, 6, J = 7.6 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 20.2 MHz) ppm 126.3 (C=CO), 125.7 (C=CO), 63.0 (CH_2O), 29.1 (CH_2), 27.0 (CH_2), 25.7 (C=CCH_2), 24.6 (CH_2), 15.2 (CH_2), 14.9 (CH_3); mass spectrum (70 eV), m/e (relative intensity) 248 (M^+, 6), 155 (79), 127 (81), 99 (100).

Anal. Calcd for $C_{11}H_{21}O_4P$: C, 53.22; H, 8.53. Found: C, 53.29; H, 8.44.

Method B. The procedure was the same as that used in method A but 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**) was added along with 0.05 equiv of tetrakis(triphenylphosphine)palladium(0). From 43 mg (0.38 mmol) of cyclohexanecarboxaldehyde, 57 mg (60%) of product (entry 17) was obtained.

Method C. Four drops of dry Me_2SO were added into a flask containing washed KH (24% in oil, 105 mg, 2.62 mmol). After the evolution of H_2 had ceased a solution of triphenylmethane (760 mg, 3.1 mmol) in freshly distilled DME (1.6 mL) was added and the mixture was heated to 40 °C for 15 min. The resulting deep red solution of tritylpotassium was cooled to 23 °C and slowly added to a solution of cyclohexanecarboxaldehyde (95 mg, 0.85 mmol) in dry DME (1.3 mL) until a permanent red color was obtained. After the mixture was stirred for 10 min at 23 °C, 3-chloro-2-[(diethoxyphosphoryl)oxy]-1-propene (**2a**, 194 mg, 0.85 mmol) was rapidly added. After stirring for 6 h at 23 °C and 10 h at 70 °C, the reaction was quenched with H_2O (10 mL). The mixture was extracted with Et_2O (4 × 20 mL), the combined ether extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Column chromatography of the crude product (silica gel 60, 60 g, 15 × 500 mm column, using 50% EtOAc in hexane as eluant) gives 65 mg (31%) of product (entry 18).

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Registry No. **2a**, 81431-81-4; **2b**, 106763-41-1; **2c**, 106763-42-2; **3**, 103647-80-9; **4**, 71712-59-9; **5a**, 41302-34-5; **5b**, 108-94-1; **6a**, 106352-32-3; **6b**, 106352-33-4; **7a**, 62359-08-4; **7b**, 6126-53-0; **8a**, 73542-61-7; **8b**, 39163-29-6; **9**, 105-45-3; **10a**, 3897-04-9; **11**, 3569-36-6; **12**, 68776-91-0; **13**, 106763-43-3; **14**, 488-10-8; **15**, 2033-24-1; **16**, 1694-31-1; **17**, 33400-61-2; **18**, 106763-44-4; **19**, 1703-51-1; **20**, 1121-05-7; **21**, 52775-77-6; **22**, 106763-45-5; **23**, 106763-46-6; **24**, 106763-47-7; **25**, 67262-88-8; **26**, 17984-82-6; **27**, 106763-48-8; **29**, 106763-49-9; **30**, 106763-50-2; **31**, 106763-51-3; 1,3-dichloroacetone, 534-07-6; allyl bromide, 106-95-6; propionyl chloride, 79-03-8; (iodomethyl)trimethylsilane, 4206-67-1; cyclohexanecarboxaldehyde, 2043-61-0; methyl acetoacetate, 105-45-3; methyl (*Z*)-1-[2-[(diethoxyphosphoryl)oxy]-4-methoxy-4-oxo-2-butenyl]-2-oxocyclohexanecarboxylate, 106763-52-4; methyl 1-[2-[(diethoxyphosphoryl)oxy]-2-propenyl]-4,4-dimethyl-2-oxocyclopentanecarboxylate, 106780-27-2; methyl 1-[2-[(diethoxyphosphoryl)oxy]-2-propenyl]-2-oxocyclopentanecarboxylate, 106763-53-5; methyl 2-acetyl-4-[(diethoxyphosphoryl)oxy]-4-pentenoate, 106763-54-6; *tert*-butyl 2-acetyl-4-[(diethoxyphosphoryl)oxy]-4-pentenoate, 106763-55-7; dimethyl 4-hydroxy-2-methyl-1,2-cyclopentadiene-1,3-dicarboxylate, 106763-56-8; 1,1-dimethylethyl 4-[(diethoxyphosphoryl)oxy]-4-pentenoate, 106763-57-9; cyclohexylidenemethyl diethyl phosphate, 106763-58-0; methyl [(trimethylsilyl)methyl]propionylacetate, 106763-59-1; methyl propionylacetate, 30414-53-0; 2-(methoxycarbonyl)-4,4-dimethylcyclopentanone, 60585-44-6; methyl 4,4-dimethyl-2-oxo-1-(2-oxopropyl)cyclopentanecarboxylate, 106763-60-4; methyl 2-oxo-1-(2-oxopropyl)cyclopentanecarboxylate, 92825-45-1.