

New Synthesis of 2-Oxo-3-alkenylphosphonates and Hetero Diels–Alder Reactions with Vinyl Ethers Leading to 5-Substituted 2-Phosphinyl-2-cyclohexen-1-ones

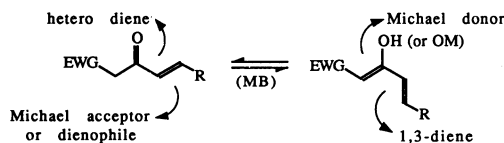
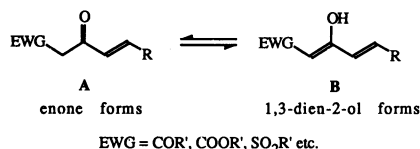
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(Received October 1, 1988)

A new method of synthesizing phosphinyl-substituted enones, 2-oxo-3-alkenylphosphonates, is developed via the dianion of diethyl 2-oxopropylphosphonate. The enones serve as hetero dienes in thermal reactions with vinyl ethers producing 2-alkoxy-6-(phosphinylmethyl)-3,4-dihydro-2*H*-pyrans. Acid-catalyzed cleavage of these cycloadducts is followed spontaneously by internal condensation furnishing 2-phosphinyl-2-cyclohexen-1-one derivatives.

It is well-known that a variety of α,β -unsaturated carbonyl compounds undergo thermal cycloadditions with electron-rich olefins such as vinyl ethers,¹⁾ enamines,²⁾ or simple alkenes³⁾ producing dihydropyran skeletons. However no reaction example has been reported so far, to the best of our knowledge, of inverse electron-demand Diels–Alder cycloadditions⁴⁾ using readily enolizable hetero dienes such as 2-oxo-3-alkenyl ketones, 3-oxo-4-alkenoates, or 2-oxo-3-alkenyl sulfones.



These hetero dienes with a general structure **A** undergo ready enolization into 1,3-dien-2-ols **B**. For example, methyl 3-oxo-4-pentenoate (**A**, EWG=COOMe, R=H) known as the Nazarov reagent⁵⁾ exists as a 1:1 mixture (¹H NMR) with enol form **B** in deuteriochloroform, and 5-hexene-2,4-dione (**A**, EWG=COMe, R=H) 1:19 (**A**:**B**) in deuteriobenzene.⁶⁾ In polar or protic medium, relative contribution of 1,3-dien-2-ols **B** must be increased. Only two examples of Diels–Alder cycloadditions of such enolized dienes **B** are known as intramolecular versions with simple olefin dienophiles.⁷⁾

We became interested in this class of compounds as reagents in the study on Diels–Alder cycloadditions. They can be utilized as highly functionalized unsaturated molecules such as hetero dienes (enone), 1,3-dienes (1,3-dien-2-ol), and dienophiles,⁸⁾ and also as annulation reagents for six-membered ring formation via Michael type cyclizations.

To open the versatility of enone reagents of type **A**, we picked up 2-oxo-3-alkenylphosphonates (**A**, EWG=(EtO)₂PO). Their new synthetic method was developed and their thermal Diels–Alder reactions with electron-rich vinyl ethers were investigated. The details are presented herein.

Results and Discussion

Syntheses of 2-Oxo-3-alkenylphosphonates **4a–f**.

The known syntheses of 2-oxo-3-alkenylphosphonates consist of hydrolysis of 2-alken-1-ynylphosphonates,⁹⁾ acylation of anions of methylphosphonates,¹⁰⁾ and dehydration of 4-hydroxy-2-oxoalkylphosphonates.¹¹⁾ As parent diethyl 2-oxo-3-butenylphosphonate (**4a**) could not be prepared¹²⁾ according to the acylation procedure reported in the literature,^{10a)} we needed another synthetic method of **4a**.¹³⁾

Several examples are known for alkylations using dianion of diethyl 2-oxopropylphosphonate (**1**)¹⁴⁾ which is readily prepared from commercially available diethyl methylphosphonate. Therefore, we planned to open to new synthetic route of 2-oxo-3-alkenylphosphonates via the dianion of **1**.

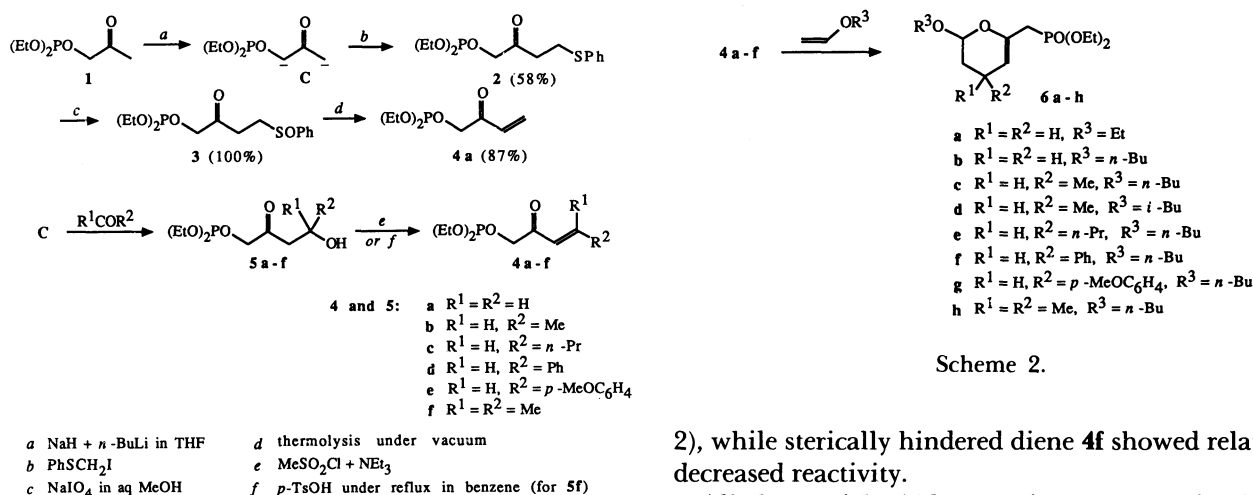
The dianion **C**, generated according to the Grieco's method by treating **1** with sodium hydride and then butyllithium (both 1.1 equiv), was reacted with phenylthiomethyl iodide to give diethyl 2-oxo-4-(phenylthio)butylphosphonate (**2**) in 58% yield (Scheme 1). Oxidation of **2** with sodium periodate led to a quantitative yield of sulfoxide **3**. The sulfoxide **3** was then subjected, without further purification, to vacuum thermolysis (at 145 °C/13 Pa) in a Kugelrohr distilling apparatus to provide **4a** as mixture with diphenyl disulfide. A repeated distillation is enough to remove the disulfide and pure **4a** was obtained in 87% yield.

Another route to **4a** is even more general. When dianion **C** was treated with paraformaldehyde in THF in the presence of a catalytic amount of hexamethylphosphoric triamide (HMPA, 1 mol%), diethyl 4-hydroxy-2-oxobutylphosphonate (**5a**) was produced.¹⁵⁾ Dehydration of **5a** leading to the enone **4a** was

Table 1. Reactions of Dianion **C**^a with Carbonyl Compounds Leading to 4-Hydroxy-2-oxoalkylphosphonates **5a–f** and 2-Oxo-3-alkenylphosphonates **4a–f**

Carbonyl compound	Condition ^b	Product (yield/%) ^c	Condition ^d	Product (yield/%) ^e
Paraformaldehyde	0°C, 4 h ^g	5a (55)	0°C, 20 min	4a (70)
MeCHO	–78°C, 1 h	5b (72)	rt, 1 h	4b (89)
<i>n</i> -PrCHO	–78°C, 30 min	5c (75)	0°C, 1 h	4c (95)
PhCHO	–78°C, 1 h	5d (83)	rt, 30 min	4d (88) ^f
<i>p</i> -MeOC ₆ H ₄ CHO	–78°C, 30 min	5e (95)	rt, 1 h	4e (86)
MeCOMe	–78°C, 1 h	5f (80)	80°C, 2 h ^g	4f (91)

a) Dianion **C** was generated in THF by treating **1** with sodium hydride (1.1 equiv, rt, 30 min) and butyllithium (1.1 equiv, –30 to –40°C, 30 min). b) 1.1 to 1.2 equivalent of a carbonyl compound was employed. c) Yields of isolated products. d) Triethylamine (3 equiv) was added at –30 to –50°C to the mixture of **5** and methanesulfonyl chloride (1.2 equiv), and the mixture was stirred under conditions listed above. e) In the presence of HMPA (0.25 equiv). f) One-flask procedure without isolation of **5d** gave 80% yield of **4d** (based on **1**). g) Under reflux in benzene with *p*-TsOH (0.5 equiv).



Scheme 1.

successfully carried out by a one-flask sequence of *O*-mesylation and β -elimination.¹¹⁾

Carbonyl compounds other than formaldehyde, such as aliphatic and aromatic aldehydes and acetone, could be employed in the condensation route with dianion **C** to give β -substituted derivatives **4b–f** in excellent yields (Scheme 1 and Table 1). Acid-catalyzed dehydration with *p*-toluenesulfonic acid (*p*-TsOH) was more effective for **5f**→**4f**.

Hetero Diels-Alder Reactions of 2-Oxo-3-alkenylphosphonates 4a–f with Vinyl Ethers. Thermally quite stable 2-oxo-3-alkenylphosphonates **4a–f** can undergo Diels-Alder cycloadditions as hetero dienes with vinyl ethers. Since their reactivity was not satisfactorily high, inexpensive vinyl ethers were employed in a large excess. The mixture of an enone **4a–f** and a vinyl ether in benzene was heated in a sealed tube at 85°C for β -unsubstituted diene **4a**, or above 130°C for other β -substituted dienes **4b–f**. In order to inhibit polymerization of vinyl ethers, a catalytic amount of *N,N*-diisopropylethylamine was added as a base.¹⁶⁾ According to these procedures, satisfactory yields of 2-alkoxy-6-(phosphinylmethyl)-3,4-dihydro-2H-pyrans **6a–h** were obtained (Scheme 2 and Table

2), while sterically hindered diene **4f** showed relatively decreased reactivity.

All these Diels-Alder reactions were regioselective like the previously observed examples,¹⁾ however stereoselectivity was poor. The isolated products **6a–h** were always the mixtures of 2,4-trans and 2,4-cis isomers in 7:3 to 6:4 ratios (¹H NMR). However, stereoisomeric purity at the 2-position is not important in the present work because 2-alkoxy-3,4-dihydro-2H-pyrans **6a–h** are to be hydrolyzed in the following step.

Reactivity of 2-oxo-3-alkenylphosphonate **4a** as a hetero diene was comparable to that of 3-buten-2-one¹⁷⁾ or even higher, indicating that ready enolization of enones does not affect their activity as hetero dienes. Even β -aryl-substituted enones **4d–e**, whose dienol forms should be more highly stabilized than others, underwent smooth cycloadditions.

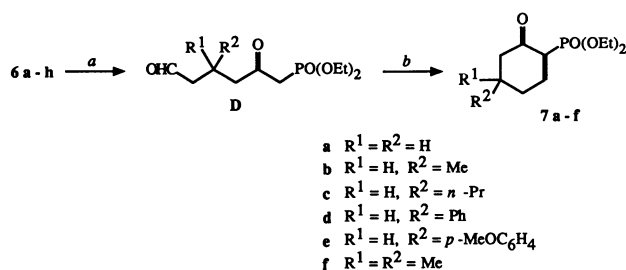
Acid-Hydrolysis and Subsequent Cyclization of the Diels-Alder Cycloadducts 6a–h. The hemiacetal moiety of 2-ethoxy-6-(diethoxyphosphorylmethyl)-3,4-dihydro-2H-pyran (**6a**) was readily hydrolyzed in 5 min at room temperature when treated with 4 M hydrochloric acid (1 M = 1 mol dm^{–3}) in THF. The unpurified product was assigned to be almost pure 6-(diethylphosphoryl)-5-oxohexanal **D** (R¹=R²=H in Scheme 3) on the basis of ¹H NMR spectrum: δ =1.33 (6H, t, *J*=7.0 Hz, OEt), 1.90 (2H, quint, *J*=7.0 Hz, 3-H), 2.50, 2.70 (each t, *J*=7.0 Hz, 2- and 4-H), 3.10

Scheme 2.

Table 2. Hetero Diels-Alder Reactions of **4a–f** with Vinyl Ethers and Subsequent Acid-Catalyzed Hydrolysis of the Cycloadducts **6a–h** Leading to 2-Phosphinyl-2-cyclohexen-1-ones **7a–f**

Heterodiene	Vinyl ether ^{a)}	Condition ^{b)}	Cycloadduct (yield/%) ^{c)}	Condition ^{d)}	Product (yield/%) ^{e)}
4a	CH ₂ =CHOEt	85 °C, 18 h	6a (83)	rt, 5 min	7a (87)
4a	CH ₂ =CHOBu- <i>n</i>	85 °C, 20 h	6b (88)	rt, 5 min	7a (92)
4b	CH ₂ =CHOBu- <i>n</i>	130–135 °C, 48 h	6c (88)	rt, 5 min	7b (89)
4b	CH ₂ =CHOBu- <i>i</i>	130–135 °C, 48 h	6d (80)		
4c	CH ₂ =CHOBu- <i>n</i>	130–135 °C, 48 h	6e (75)	rt, 5 min	7c (85)
4d	CH ₂ =CHOBu- <i>n</i>	130–135 °C, 96 h	6f (66)	rt, 10 min	7d (79)
4e	CH ₂ =CHOBu- <i>n</i>	140–145 °C, 72 h	6g (81)	rt, 15 min	7e (84)
4f	CH ₂ =CHOBu- <i>n</i>	170–185 °C, 72 h	6h (57) ^{a)}	rt, 10 min	7f (72)

a) Twenty equivalents of a vinyl ether were employed. b) All reactions were carried out in benzene in a sealed tube in the presence of a catalytic amount of *N,N*-diisopropylethylamine. c) Yields of isolated products. d) In THF with 4 M hydrochloric acid (2:1 v/v). e) 12% Yield of **4f** was recovered.



a) 4M-HCl in THF at rt
b) silica-gel chromatography

Scheme 3.

(2H, d $J_{\text{C-P}}=22.5$ Hz, 6-H), 4.20 (4H, dq $J=7.0$ and $J_{\text{C-P}}=7.7$ Hz, OEt), and 9.77 (1H, br s, CHO).

It was found that aldehyde **D** ($\text{R}^1=\text{R}^2=\text{H}$) underwent smooth cyclization leading to 2-(diethoxyphosphoryl)-2-cyclohexen-1-one (**7a**) in 87% yield on its attempted purification through column chromatography on silica gel. Presumably such a weak acid as silica gel is requisite in this facile cyclization since intermediate **D** ($\text{R}^1=\text{R}^2=\text{H}$) was found stable in 4 M hydrochloric acid as mentioned above. With a more diluted hydrochloric acid, the hydrolysis of **5a** becomes slower and instead the acid-catalyzed cyclization of **D** is relatively accelerated, isolation of the intermediate aldehyde **D** in a pure form becoming more difficult.

Other 2-alkoxy-3,4-dihydro-2H-pyrans **4b–f** were hydrolyzed under similar conditions and crude reaction mixtures were subjected to silica-gel chromatography to give 2-phosphinyl-2-cyclohexen-1-ones **7b–f** in satisfactory yields (Scheme 3 and Table 2).

Although acyclic vinylphosphonates bearing an acyl or ester moiety at the 1-position have been synthesized by the secondary amine-promoted condensation of phosphonates¹⁸⁾ or the β -elimination¹⁹⁾ of 1-sulfinyl phosphonates, synthetic example of 1-cycloalkenylphosphonates is quite limited.^{20,21)} The present reactions offer a high-yield and short step synthesis of 2-phosphinyl-2-cyclohexen-1-ones bearing a substituent at the 5-position.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ¹H NMR spectra were recorded on a Hitachi R-40 (90 MHz), a JEOL FX-100 (100 MHz), or a JEOL GSX-270 instrument (270 MHz), and ¹³C NMR on a JEOL FX-100 (25.05 MHz) or a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN analyzer. For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04–0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Materials. Compounds **4d** and **5d** were previously prepared and characterized.³⁾ Though compounds **4a**, **4b**, **4f** are all known,^{10a)} refractive indexes, ¹H NMR spectra without coupling constants, and boiling points are the only reported data. Accordingly full data of these compounds are presented below. Triethylamine and dichloromethane were purified by distillation on potassium hydroxide and calcium hydride, respectively. Tetrahydrofuran (THF) was distilled on lithium aluminum hydride under nitrogen prior to use.

Diethyl 2-Oxo-4-(phenylthio)butylphosphonate (2). To a suspension of sodium hydride (60% in mineral oil, 0.93 g, 22 mol) in dry THF (60 ml) was added diethyl 2-oxopropylphosphonate (**1**, 3.88 g, 20 mmol) under nitrogen. After 30 min at room temperature, butyllithium (in hexane, 13 ml, 23 mmol) was added at –5 °C. The mixture was stirred at room temperature for 30 min and phenylthiomethyl iodide

(4.5 g, 18 mmol) was added. After stirring was continued at -10 to -5 °C for 2 h, the mixture was poured into ice-cold 3 M hydrochloric acid and then extracted with diethyl ether (30 ml $\times$ 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane-ethyl acetate (1:2 v/v) to give **2** (3.32 g, 58%): Pale yellow liquid; IR (neat) 1710, 1580, 1475, 1440, 1250, 1050, 1015, 960, 800, 740, and 690 cm^{-1} ; ^1H NMR (CDCl_3) δ =1.31 (6H, t, J =7.0 Hz, EtO), 2.95 (2H, t, J_{3-4} =6.9 Hz, 3-H), 3.07 (2H, d, $J_{\text{H-P}}$ =22.7 Hz, 1-H), 3.14 (2H, t, J_{4-3} =6.9 Hz, 4-H), 4.12 (4H, quint, J = $J_{\text{H-P}}$ =7.0 Hz, EtO), and 7.2–7.4 (5H, m, Ph); ^{13}C NMR (CDCl_3) δ =16.28 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 27.36 (4-C), 42.59 (d, $J_{\text{C-P}}$ =127.1 Hz, 1-C), 43.58 (3-C), 62.66 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 126.39, 129.03, 129.63, 135.58 (each Ph), and 200.11 (d, $J_{\text{C-P}}$ =5.9 Hz, CO); MS m/z (rel intensity, %) 316 (M^+ , 31), 207 (base peak), 179 (40), 152 (26), 151 (44), 125 (39), 123 (35), 110 (21), 109 (35), and 97 (10). HRMS Found: m/z 316.0754. Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{P}$: M, 316.0897.

Oxidation of 2 with Sodium Periodate and Subsequent Thermolysis of 3 Leading to 4a. To a solution of **2** (1.8 g 5.69 mmol) in methanol (35 ml) was added aqueous sodium periodate (1.95 g, 9.1 mmol in 13 ml of water) at -10 to 0 °C. The mixture was stirred at 0 °C for 4 h and extracted with chloroform (25 ml). The extract was dried over magnesium sulfate and evaporated in vacuo. The crude sulfoxide **3** (1.9 g, 100%) was heated at 145 °C under vacuum (27 Pa) in a Kugelrohr distilling apparatus. The distillate (1.4 g) was purified by vacuum distillation to give **4a** (bp 130 °C/13 Pa, 1.13 g, 87%). The data of **4a** are presented below.

General Procedure for the Preparation of Diethyl 4-Hydroxy-2-oxoalkylphosphonates 5a–f. As a typical example the preparation of **5a** is described as follows: To the THF solution of dianion **C** freshly prepared from **1** (3.88 g, 20 mmol) according to the method mentioned above were added at -78 °C paraformaldehyde (0.6 g, 20 mmol) and hexamethylphosphoric triamide (HMPA, 0.1 ml). After stirred at 0 °C for 4 h, the mixture was acidified with 1 M hydrochloric acid. The THF was removed in vacuo and the aqueous residue was extracted with dichloromethane (40 ml $\times$ 4). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The crude product (4.6 g) was chromatographed over silica gel with ethyl acetate-methanol (99.5:0.5 to 96:4 v/v) to give **5a** (2.45 g, 55%). No HMPA was needed in the preparation of other derivatives **5b–f**; the reaction conditions and the results are summarized in Table 1. Eluents used in the chromatographic purification are as follows: **5b**, **5c**, and **5e**: ethyl acetate-methanol (95:5 v/v); **5d**: ethyl acetate; **5f**: ethyl acetate-methanol (98:2 v/v).

Diethyl 4-Hydroxy-2-oxobutylphosphonate (5a): Colorless liquid; IR (neat) 3400, 1710, 1240, 1020, and 800 cm^{-1} ; ^1H NMR (CDCl_3) δ =1.32 (6H, t, J =7.0 Hz, EtO), 2.83 (2H, t, J_{3-4} =6.0 Hz, 3-H), 3.14 (2H, d, $J_{\text{H-P}}$ =23.0 Hz, 1-H), 3.48 (1H, br s, OH), 3.48 (2H, t, J_{4-3} =6.0 Hz, 4-H), and 4.12 (4H, dq, J =7.0 and $J_{\text{H-P}}$ =8.0 Hz, EtO); ^{13}C NMR (CDCl_3) δ =16.32 (qd, $J_{\text{C-P}}$ =7.4 Hz, EtO), 42.65 (td, $J_{\text{C-P}}$ =126.5 Hz, 1-C), 46.77 (t, 3-C), 57.47 (t, 4-C), 62.83 (td, $J_{\text{C-P}}$ =5.9 Hz, EtO), and 202.30 (d, $J_{\text{C-P}}$ =5.9 Hz, CO); MS m/z (rel intensity, %) 224 (M^+ , 5), 194 (base peak), 179 (45), 152 (44), 151 (42), 125 (67), 123 (57), 109 (32), 108 (20), 97 (41), 81 (28), and 43 (28). HRMS Found: m/z 224.0808. Calcd for $\text{C}_8\text{H}_{17}\text{O}_5\text{P}$: M, 224.0813.

Diethyl 4-Hydroxy-2-oxopentylphosphonate (5b): Colorless liquid; IR (neat) 3400, 1710, 1245, 1050, 1020, 960, and 790 cm^{-1} ; ^1H NMR (CDCl_3) δ =1.24 (3H, d, J_{5-4} =6.7 Hz, 5-H), 1.35 (6H, t, J =7.0 Hz, EtO), 2.76 (1H, d, J_{3-4} =6.4 Hz, one of 3-H), 2.74 (1H, d, J_{3-4} =5.5 Hz, the other of 3-H), 3.17 (2H, d, $J_{\text{H-P}}$ =22.9 Hz, 1-H), 3.66 (1H, br d, J =4.0 Hz, OH), 4.16 (4H, dq, J =7.0 and $J_{\text{H-P}}$ =8.1 Hz, EtO), and 4.0–4.3 (1H, m, 4-H); ^{13}C NMR (CDCl_3) δ =16.26 (dq, $J_{\text{C-P}}$ =5.9 Hz, EtO), 22.76 (q, 5-C), 43.38 (dt, $J_{\text{C-P}}$ =126.0 Hz, 1-C), 52.59 (t, 3-C), 62.60 (dt, $J_{\text{C-P}}$ =5.9 Hz, EtO), 63.77 (d, 4-C), and 202.19 (d, $J_{\text{C-P}}$ =5.9 Hz, CO); MS m/z (rel intensity, %) 238 (M^+ , 3), 223 (25), 195 (27), 194 (base peak), 179 (31), 167 (21), 152 (34), 151 (22), 139 (20), 125 (44), 123 (33), 97 (25), 81 (21), and 43 (20). HRMS Found: m/z 238.0963. Calcd for $\text{C}_9\text{H}_{19}\text{O}_5\text{P}$: M, 238.0969.

Diethyl 4-Hydroxy-2-oxoheptylphosphonate (5c): Colorless liquid; IR (neat) 3400, 1710, 1395, 1250, 1050, 1020, 975, and 800 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.92 (3H, t, J_{7-6} =7.0 Hz, 7-H), 1.34 (6H, t, J =7.0 Hz, EtO), 1.3–1.6 (4H, m, 5- and 6-H), 2.70 (1H, dd, J_{gem} =17.2 and J_{3-4} =8.4 Hz, one of 3-H), 2.80 (1H, dd, J_{gem} =17.2 and J_{3-4} =3.7 Hz, the other of 3-H), 3.10 (1H, dd, J_{gem} =13.0 and $J_{\text{H-P}}$ =22.7 Hz, one of 1-H), 3.19 (1H, dd, J_{gem} =13.0 and $J_{\text{H-P}}$ =22.7 Hz, the other of 1-H), 3.35 (1H, br s, OH), 4.07 (1H, m, 4-H), and 4.15 (4H, dq, J =7.0 and $J_{\text{H-P}}$ =8.1 Hz, EtO); ^{13}C NMR (CDCl_3) δ =13.98 (7-C), 16.33 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 18.68 (6-C), 38.89 (5-C), 43.09 (d, $J_{\text{C-P}}$ =127.2 Hz, 1-C), 51.16 (3-C), 62.76 (d, $J_{\text{C-P}}$ =6.9 Hz, EtO), 67.38 (4-C), and 202.89 (d, $J_{\text{C-P}}$ =5.9 Hz, CO); MS m/z (rel intensity, %) 266 (M^+ , 5), 222 (base peak), 195 (34), 194 (43), 179 (20), 139 (20), 125 (23), 123 (20), and 97 (13). HRMS Found: m/z 266.1320. Calcd for $\text{C}_{11}\text{H}_{23}\text{O}_5\text{P}$: M, 266.1320.

Diethyl 4-Hydroxy-4-(*p*-methoxyphenyl)-2-oxobutylphosphonate (5e): Colorless liquid; IR (neat) 3350, 1705, 1610, 1580, 1505, 1300, 1250, 1175, 1025, 960, 825, and 790 cm^{-1} ; ^1H NMR (CDCl_3) δ =1.32 (6H, t, J =6.6 Hz, EtO), 2.92 (1H, dd, J_{gem} =17.2 and J_{3-4} =3.7 Hz, one of 3-H), 3.05 (1H, dd, J_{gem} =17.2 and J_{3-4} =8.8 Hz, the other of 3-H), 3.07 (1H, dd, J_{gem} =13.5 and $J_{\text{H-P}}$ =22.7 Hz, one of 1-H), 3.16 (1H, dd, J_{gem} =13.5 and $J_{\text{H-P}}$ =22.7 Hz, the other of 1-H), 3.65 (1H, br, OH), 4.12 (4H, m, EtO), 5.11 (1H, dd, J_{4-3} =8.8 and 3.7 Hz, 4-H), 6.86 (2H, dt, J =8.4 and 1.8 Hz, Ar), and 7.28 (2H, dt, J =8.4 and 1.8 Hz, Ar); ^{13}C NMR (CDCl_3) δ =16.30 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 43.11 (d, $J_{\text{C-P}}$ =127.0 Hz, 1-C), 52.87 (3-C), 55.28 (*p*-MeO), 62.73 (d, $J_{\text{C-P}}$ =6.9 Hz, EtO), 69.50 (4-C), 113.86, 126.97, 135.17, 159.10 (each Ar), and 201.98 (d, $J_{\text{C-P}}$ =5.9 Hz, CO); MS m/z (rel intensity, %) 330 (M^+ , 19), 195 (32), 194 (85), 167 (29), 161 (44), 152 (47), 150 (20), 139 (26), 137 (37), 136 (25), 135 (base peak), 125 (63), 123 (28), 109 (31), 96 (42), 80 (31), 76 (31), and 43 (33). HRMS Found: m/z 330.1235. Calcd for $\text{C}_{15}\text{H}_{23}\text{O}_6\text{P}$: M, 330.1231.

Diethyl 4-Hydroxy-4-methyl-2-oxopentylphosphonate (5f): Colorless liquid; IR (neat) 3400, 1705, 1470, 1440, 1380, 1350, 1320, 1240, 1155, 1040, 1020, 970, and 780 cm^{-1} ; ^1H NMR (CDCl_3) δ =1.27 (6H, s, 5-H and 4-Me), 1.35 (6H, t, J =7.0 Hz, EtO), 2.82 (2H, s, 3-H), 3.14 (2H, d, $J_{\text{H-P}}$ =22.7 Hz, 1-H), 3.70 (1H, br, OH), and 4.15 (4H, dq, J =7.0 and $J_{\text{H-P}}$ =8.1 Hz, EtO); ^{13}C NMR (CDCl_3) δ =16.31 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 29.33 (5- and 4-Me), 43.83 (d, $J_{\text{C-P}}$ =126.2 Hz, 1-C), 55.09 (3-C), 62.69 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 69.67 (4-C), and 203.55 (d, $J_{\text{C-P}}$ =5.9 Hz, CO); MS m/z (rel intensity, %) 253 (M^+ +1, 5), 237 (91), 195 (25), 194 (94), 179 (47), 167 (49), 152 (49), 151 (36), 139 (77), 125 (81), 124 (22), 123 (77), 121 (41), 109 (37), 108 (20), 105

(22), 97 (63), 96 (43), 81 (61), 78 (24), 65 (33), 59 (73), 58 (21), and 43 (base peak). No analytical data was obtained because of the absence of parent ion peak and the hygroscopic nature.

General Procedure for the Dehydration of 5a–f Leading to 2-Oxo-3-alkenylphosphonates 4a–f. As a typical example the conversion of **5a** into **4a** is described as follows: To a solution of **5a** (5.15 g, 23 mmol) and methanesulfonyl chloride (3.16 g, 27.6 mmol) in dry dichloromethane (50 ml) was added dropwise triethylamine (6.91 g, 68.9 mmol) at -50°C . After stirring at 0°C for 20 min, the mixture was poured into ice water. The dichloromethane separated was washed with 1 M hydrochloric acid and water, dried over magnesium sulfate, and then evaporated in vacuo. The crude product (4.4 g) was subjected to vacuum distillation to give **4a** (3.3 g, 70%). Other compounds **5b–e** were similarly dehydrated under the reaction conditions listed in Table 1. Eluents used for the chromatographic purification of **4b–e** are as follows: **4b**: hexane–ethyl acetate (1:1 to 0:1 v/v); **4c**: ethyl acetate; **4d**: hexane–ethyl acetate (1:2 v/v); **4e**: hexane–ethyl acetate (1:4 to 0:1 v/v).

Diethyl 2-Oxo-3-butenylphosphonate (4a):^{10a} Colorless liquid; bp $130^{\circ}\text{C}/13\text{ Pa}$ (bulb-to-bulb); IR (neat) 1670, 1610, 1240, 1020, and 800 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=1.32$ (6H, t, $J=7.0\text{ Hz}$, EtO), 3.24 (2H, d, $J_{\text{H-P}}=22.5\text{ Hz}$, 1-H), 4.12 (4H, dd, $J=7.0$ and $J_{\text{H-P}}=8.0\text{ Hz}$, EtO), 5.90 (1H, dd, $J_{4-3(\text{cis})}=9.0$ and $J_{\text{gem}}=2.5\text{ Hz}$, one of 4-H), 6.26 (1H, dd, $J_{4-3(\text{trans})}=17.5$ and $J_{\text{gem}}=2.5\text{ Hz}$, the other of 4-H), and 6.50 (1H, dd, $J_{3-4(\text{trans})}=17.5$ and $J_{4-3(\text{cis})}=9.0\text{ Hz}$, 3-H); $^{13}\text{C NMR}$ (CDCl_3) $\delta=16.35$ (qd, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 39.88 (td, $J_{\text{C-P}}=129.4\text{ Hz}$, 1-C), 62.71 (td, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 130.60 (t, 4-C), 136.42 (d, 3-C), and 192.04 (s, 2-C); MS m/z (rel intensity, %) 206 (M^+ , 79), 179 (35), 178 (35), 161 (34), 151 (70), 134 (33), 133 (34), 125 (60), 123 (73), 109 (48), 97 (52), 96 (22), 81 (33), 70 (31), and 55 (base peak). HRMS Found: m/z 206.0698. Calcd for $\text{C}_8\text{H}_{15}\text{O}_4\text{P}$: M, 206.0707.

Diethyl (E)-2-Oxo-3-pentenylphosphonate (4b):^{10a} Colorless liquid; bp $145\text{--}150^{\circ}\text{C}/20\text{ Pa}$ (bulb-to-bulb); IR (neat) 1660, 1625, 1440, 1290, 1245, 1050, 1020, 960, and 940 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=1.33$ (6H, t, $J=7.0\text{ Hz}$, EtO), 1.94 (3H, br d, $J_{5-4}=6.9\text{ Hz}$, 5-H), 3.19 (2H, d, $J_{\text{H-P}}=22.7\text{ Hz}$, 1-H), 4.14 (4H, dq, $J=7.0$ and $J_{\text{H-P}}=8.1\text{ Hz}$, EtO), 6.26 (1H, br d, $J_{3-4}=15.8\text{ Hz}$, 3-H), and 6.96 (1H, br dq, $J_{4-3}=15.8$ and $J_{4-5}=6.9\text{ Hz}$, 4-H); $^{13}\text{C NMR}$ (CDCl_3) $\delta=16.31$ (d, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 18.37 (5-C), 40.06 (d, $J_{\text{C-P}}=123.3\text{ Hz}$, 1-C), 62.56 (d, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 131.72 (3-C), 145.58 (4-C), and 191.10 (d, $J_{\text{C-P}}=6.9\text{ Hz}$, CO); MS m/z (rel intensity, %) 220 (M^+ , 22), 125 (35), 97 (30), 69 (base peak), and 41 (49). HRMS Found: m/z 220.0863. Calcd for $\text{C}_9\text{H}_{17}\text{O}_4\text{P}$: M, 220.0863.

Diethyl (E)-2-Oxo-3-heptenylphosphonate (4c): Colorless liquid; bp $150^{\circ}\text{C}/27\text{ Pa}$ (bulb-to-bulb); IR (neat) 1690, 1665, 1625, 1250, 1055, 1025, 975, and 790 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=0.95$ (3H, t, $J_{7-6}=7.4\text{ Hz}$, 7-H), 1.33 (6H, t, $J=7.0\text{ Hz}$, EtO), 1.52 (2H, sex, $J_{6-5}=J_{6-7}=7.4\text{ Hz}$, 6-H), 2.24 (2H, br q, $J_{5-4}=J_{5-6}=7.4\text{ Hz}$, 5-H), 3.21 (2H, d, $J_{\text{H-P}}=22.7\text{ Hz}$, 1-H), 4.14 (4H, dq, $J=7.0$ and $J_{\text{H-P}}=8.1\text{ Hz}$, EtO), 6.24 (1H, br d, $J_{3-4}=15.8\text{ Hz}$, 3-H), and 6.95 (1H, br dt, $J_{4-3}=15.8$ and $J_{4-5}=7.4\text{ Hz}$, 4-H); $^{13}\text{C NMR}$ (CDCl_3) $\delta=13.68$ (7-C), 16.32 (d, $J_{\text{C-P}}=6.8\text{ Hz}$, EtO), 21.25 (6-C), 34.54 (5-C), 40.12 (d, $J_{\text{C-P}}=128.1\text{ Hz}$, 1-C), 62.52 (d, $J_{\text{C-P}}=6.8\text{ Hz}$, EtO), 130.22 (3-C), 150.25 (4-C), and 191.31 (d, $J_{\text{C-P}}=5.9\text{ Hz}$, CO); MS m/z (rel intensity, %) 248 (M^+ , base peak), 220 (33), 179 (27), 152

(30), 151 (27), 125 (39), 123 (34), 110 (26), 97 (34), and 55 (33). HRMS Found: m/z 248.1191. Calcd for $\text{C}_{11}\text{H}_{21}\text{O}_4\text{P}$: M, 248.1176.

Diethyl (E)-4-(p-Methoxyphenyl)-2-oxo-3-butenylphosphonate (4e): Colorless prisms (diethyl ether–hexane); mp $53\text{--}54^{\circ}\text{C}$; IR (KBr) 1675, 1640, 1595, 1295, 1250, 1175, 1075, 1050, 1025, 960, and 840 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=1.33$ (6H, t, $J=7.0\text{ Hz}$, EtO), 3.30 (2H, d, $J_{\text{H-P}}=22.7\text{ Hz}$, 1-H), 3.84 (3H, s, *p*-MeO), 4.17 (4H, dq, $J=7.0$ and $J_{\text{H-P}}=8.1\text{ Hz}$, EtO), 6.77 (1H, br d, $J_{3-4}=16.1\text{ Hz}$, 3-H), 6.91 (2H, br d, $J=8.9\text{ Hz}$, Ar), 7.53 (2H, br d, $J=8.9\text{ Hz}$, Ar), and 7.61 (1H, br d, $J_{4-3}=16.1\text{ Hz}$, 4-H); $^{13}\text{C NMR}$ (CDCl_3) $\delta=16.36$ (d, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 40.93 (d, $J_{\text{C-P}}=128.1\text{ Hz}$, 1-C), 55.42 (*p*-MeO), 62.58 (d, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 114.50, 123.60, 126.88, 130.42, 144.60, 161.98 (Ar, 3- and 4-C), and 190.91 (d, $J_{\text{C-P}}=5.9\text{ Hz}$, CO); MS m/z (rel intensity, %) 312 (M^+ , 24), 174 (56), 161 (base peak), and 133 (18). Found: C, 57.71; H, 7.01%. Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_5\text{P}$: C, 57.69; H, 6.78%.

Diethyl 4-Methyl-2-oxo-3-pentenylphosphonate (4f):^{10a} A solution of **5f** (1.008 g, 4 mmol) and *p*-toluenesulfonic acid monohydrate (0.38 g, 2 mmol) in benzene (30 ml) was heated under reflux for 2 h with continuous removal of water by the aid of a Dean–Stark trap. The mixture was evaporated in vacuo, the residue was washed with water, and extracted with dichloromethane (25 ml $\times$ 2). The combined extracts were washed with saturated aqueous sodium hydrogencarbonate, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed over silica gel with dichloromethane–ethyl acetate (2:1 v/v) to give **4f** (0.85 g, 91%): Colorless liquid; bp $150^{\circ}\text{C}/27\text{ Pa}$ (bulb-to-bulb); IR (neat) 1680, 1620, 1445, 1390, 1250, 1025, 965, and 790 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=1.33$ (6H, t, $J=7.0\text{ Hz}$, EtO), 1.92, 2.16 (each 3H, s, 5-H and 4-Me), 3.07 (2H, d, $J_{\text{H-P}}=22.7\text{ Hz}$, 1-H), 4.14 (4H, dq, $J=7.0$ and $J_{\text{H-P}}=8.1\text{ Hz}$, EtO), and 6.25 (1H, s, 3-H); $^{13}\text{C NMR}$ (CDCl_3) $\delta=16.32$ (d, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 21.02 (5-C), 27.79 (4-Me), 43.70 (d, $J_{\text{C-P}}=127.2\text{ Hz}$, 1-C), 62.42 (d, $J_{\text{C-P}}=5.9\text{ Hz}$, EtO), 123.93 (3-C), 158.04 (4-C), and 190.85 (d, $J_{\text{C-P}}=5.9\text{ Hz}$, 2-C); MS m/z (rel intensity, %) 234 (M^+ , 17), 97 (23), 96 (61), 83 (base peak), 81 (34), 59 (66), and 58 (26).

General Procedure for the Hetero Diels–Alder Reaction of 4a–f Leading to 3,4-Dihydro-2H-pyrans 6a–h. As a typical procedure the reaction of **4a** with ethyl vinyl ether is described as follows: A mixture of **4a** (1.035 g, 5.02 mmol), ethyl vinyl ether (7.2 g, 100 mmol), and *N,N*-diisopropylethylamine (trace) in benzene (1 ml) was heated in a sealed tube at 85°C for 18 h. The mixture was condensed in vacuo and the residue was chromatographed over silica gel by using ethyl acetate–methanol (1:0 to 98:2 v/v) to give **6a** (1.16 g, 83%). Other cycloadducts **6b–h** were similarly obtained under the reaction conditions listed in Table 2. Eluents used for the chromatographic purification are as follows: **6b**: hexane–ethyl acetate (1:2 to 0:1 v/v); **6c** and **6d**: dichloromethane–ethyl acetate (2:1 to 2:3 v/v); **6e** and **6h**: hexane–ethyl acetate (1:2 v/v); **6f**: hexane–ethyl acetate (2:3 v/v); **6g**: dichloromethane–ethyl acetate (3:1 v/v); No satisfactory analytical data were obtained because of the hygroscopic nature of **6a–h**. Analysis by HRMS was carried out for the stereochemically pure **6a, b**. The other compounds **6c–h** were characterized on the basis of spectral data and employed for the following reactions.

2-Ethoxy-6-[(diethoxyphosphoryl)methyl]-3,4-dihydro-2H-

pyran (6a): Colorless liquid; IR (neat) 1675, 1475, 1440, 1380, 1240, 1155, 1110, 1050, 1025, and 955 cm^{-1} ; ^1H NMR (C_6D_6) δ =1.10 (6H, dt, J =7.0 and $J_{\text{H-P}}$ =4.0 Hz, EtO), 1.14 (3H, t, J =7.0 Hz, 2-EtO), 1.5–1.8 (3H, m, 3- and 4-H), 2.17 (1H, m, one of 3-H), 2.60 (2H, d, $J_{\text{H-P}}$ =20.9 Hz, 6- CH_2P), 3.43 (1H, dq, J_{gem} =9.5 and J =7.0 Hz, 2-EtO), 3.9–4.1 (1H, m, 2-EtO), 4.13 (4H, dq, J =7.0 and $J_{\text{H-P}}$ =8.1 Hz, EtO), 4.73 (1H, br q, J_{5-4} = $J_{\text{H-P}}$ =4.4 Hz, 5-H), and 4.88 (1H, t, J_{2-3} =3.3 Hz, 2-H); ^{13}C NMR (C_6D_6) δ =15.33 (2-EtO), 16.53, 16.56 (each d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 17.32 (4-C), 26.58 (3-C), 32.94 (d, $J_{\text{C-P}}$ =139.9 Hz, 6- CH_2P), 61.61, 61.81 (each d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 63.79 (2-EtO), 97.71 (2-C), 99.88 (d, $J_{\text{C-P}}$ =9.8 Hz, 5-C), and 143.14 (d, $J_{\text{C-P}}$ =10.8 Hz, 6-C); MS m/z (rel intensity, %) 278 (M^+ , 45), 233 (37), 232 (base peak), 231 (49), 207 (30), 203 (65), 151 (33), 140 (30), 123 (24), 95 (42), 94 (61), and 72 (42). HRMS Found: m/z 278.1284. Calcd for $\text{C}_{12}\text{H}_{23}\text{O}_5\text{P}$: M , 278.1282.

2-Butoxy-6-[(diethoxyphosphoryl)methyl]-3,4-dihydro-2H-pyran (6b): Colorless liquid; IR (neat) 1675, 1445, 1390, 1360, 1250, 1120, 1030, 965, 840, 805, and 790 cm^{-1} ; ^1H NMR (C_6D_6) δ =0.87 (3H, t, J =7.0 Hz, *n*-BuO), 1.10 (6H, dt, J =7.0 and $J_{\text{H-P}}$ =4.4 Hz, EtO), 1.38 (2H, m, *n*-BuO), 1.55 (2H, m, *n*-BuO), 1.5–1.8 (3H, m, 3- and 4-H), 2.15 (1H, m, one 3-H), 2.62 (2H, d, $J_{\text{H-P}}$ =20.9 Hz, 6- CH_2P), 3.41 (1H, dt, J_{gem} =9.5 and J =6.5 Hz, *n*-BuO), 3.9–4.1 (5H, m, EtO and *n*-BuO), 4.74 (1H, q, J_{5-4} = $J_{\text{H-P}}$ =4.0 Hz, 5-H), and 4.89 (1H, t, J_{2-3} =3.4 Hz, 2-H); ^{13}C NMR (C_6D_6) δ =14.10 (*n*-BuO), 16.54, 16.57 (each d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 17.35 (d, $J_{\text{C-P}}$ =2.1 Hz, 4-C), 19.73 (*n*-BuO), 26.59 (3-C), 32.18 (*n*-BuO), 32.96 (d, $J_{\text{C-P}}$ =140.9 Hz, 6- CH_2P), 61.58, 61.77 (each d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 68.17 (*n*-BuO), 97.92 (2-C), 99.85 (d, $J_{\text{C-P}}$ =9.6 Hz, 5-C), and 143.18 (d, $J_{\text{C-P}}$ =10.8 Hz, 6-C); MS m/z (rel intensity, %) 306 (M^+ , 28), 233 (29), 232 (base peak), 231 (34), 207 (26), 203 (55), 179 (26), 151 (32), 123 (23), 95 (28), 94 (55), and 56 (23). HRMS Found: m/z 306.1635. Calcd for $\text{C}_{14}\text{H}_{27}\text{O}_5\text{P}$: 306.1595.

2-Butoxy-6-[(diethoxyphosphoryl)methyl]-4-methyl-3,4-dihydro-2H-pyran (6c): A 34:66 mixture of cis and trans isomers (^{13}C NMR); Colorless liquid; IR (neat) 1675, 1450, 1390, 1370, 1325, 1295, 1250, 1120, 1050, 1020, 960, 830, and 770 cm^{-1} ; ^1H NMR (C_6D_6) cis: δ =0.87 (3H, t, J =7.3 Hz, *n*-BuO), 0.92 (3H, d, J =6.6 Hz, 4-Me), 1.11 (6H, dt, J =7.0 and $J_{\text{H-P}}$ =1.5 Hz, EtO), 1.2–1.7 (5H, m, 3-H and *n*-BuO), 1.83 (1H, dddd, J_{gem} =13.2, J_{3-4} =6.0, J_{3-2} =2.2, and J_{3-5} =1.0 Hz, one of 3-H), 2.19 (1H, m, 4-H), 2.57 (1H, dd, J_{gem} =15.0 and $J_{\text{H-P}}$ =21.0 Hz, one of 6- CH_2P), 2.65 (1H, dd, J_{gem} =15.0 and $J_{\text{H-P}}$ =21.0 Hz, the other of 6- CH_2P), 3.42 (1H, dt, J_{gem} =9.5 and J =6.8 Hz, *n*-BuO), 4.01 (4H, quint, J = $J_{\text{H-P}}$ =7.0 Hz, EtO), 4.01 (1H, dt, J_{gem} =9.5 and J =6.8 Hz, *n*-BuO), 4.57 (1H, m, 5-H), and 4.86 (1H, dd, J_{2-3} =8.1 and 2.2 Hz, 2-H); trans: δ =0.87 (3H, t, J =7.0 Hz, *n*-BuO), 0.87 (3H, d, J =6.6 Hz, 4-Me), 1.10 (6H, br d, J =7.0 Hz, EtO), 1.2–1.7 (5H, m, 3-H and *n*-BuO), 1.7–1.9 (1H, m, one of 3-H), 2.52 (1H, m, 4-H), 2.5–2.7 (2H, m, 6- CH_2P), 3.3–3.4 (1H, m, *n*-BuO), 3.9–4.1 (5H, m, *n*-BuO and EtO), 4.65 (1H, m, 5-H), and 4.93 (1H, t, J_{2-3} =3.0 Hz, 2-H); ^{13}C NMR (C_6D_6) cis: δ =14.05 (*n*-BuO), 16.56 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 19.70 (*n*-BuO), 21.58 (d, $J_{\text{C-P}}$ =2.9 Hz, 4-Me), 26.69 (d, $J_{\text{C-P}}$ =2.0 Hz, 4-C), 32.20 (*n*-BuO), 32.69 (d, $J_{\text{C-P}}$ =139.9 Hz, 6- CH_2P), 36.30 (3-C), 61.77 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 68.67 (*n*-BuO), 100.40 (2-C), 105.93 (d, $J_{\text{C-P}}$ =9.8 Hz, 5-C), and 143.29 (d, $J_{\text{C-P}}$ =10.8 Hz, 6-C); trans: δ =14.13 (*n*-BuO), 16.59 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 19.76 (*n*-BuO), 21.40

(d, $J_{\text{C-P}}$ =2.9 Hz, 4-Me), 22.68 (d, $J_{\text{C-P}}$ =2.0 Hz, 4-C), 32.22 (*n*-BuO), 32.89 (d, $J_{\text{C-P}}$ =139.9 Hz, 6- CH_2P), 35.19 (3-C), 61.57 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 68.19 (*n*-BuO), 97.51 (2-C), 106.68 (d, $J_{\text{C-P}}$ =9.8 Hz, 5-C), and 142.23 (d, $J_{\text{C-P}}$ =10.8 Hz, 6-C); MS m/z (rel intensity, %) 320 (M^+ , 34), 247 (35), 246 (86), 245 (36), 231 (91), 221 (74), 217 (29), 123 (40), 110 (25), 108 (base peak), 58 (22), and 57 (28).

6-[(Diethoxyphosphoryl)methyl]-2-isobutoxy-4-methyl-3,4-dihydro-2H-pyran (6d): A 38:62 mixture of cis and trans isomers (^{13}C NMR); Colorless liquid; IR (neat) 1675, 1450, 1390, 1365, 1250, 1120, 1050, 1020, 975, 895, 830, and 775 cm^{-1} ; ^1H NMR (C_6D_6) cis: δ =0.92 (6H, d, J =7.0 Hz, *i*-BuO), 0.93 (3H, t, J =7.0 Hz, 4-Me), 1.11 (6H, dt, J =7.0 and $J_{\text{H-P}}$ =1.5 Hz, EtO), 1.49 (1H, ddd, J_{gem} =13.2, J_{3-4} =9.2, and J_{3-2} =8.1 Hz, one of 3-H), 1.82 (1H, m, the other of 3-H), 1.88 (1H, m, *i*-BuO), 2.20 (1H, m, 4-H), 2.57, 2.65 (each 1H, dd, J_{gem} =13.5 and $J_{\text{H-P}}$ =21.0 Hz, 6- CH_2P), 3.18, 3.81 (each 1H, dd, J_{gem} =9.5 and J =7.0 Hz, *i*-BuO), 4.01 (4H, dq, J =7.0 and $J_{\text{H-P}}$ =8.1 Hz, EtO), 4.58 (1H, m, 5-H), and 4.85 (1H, dd, J_{2-3} =8.1 and 2.2 Hz, 2-H); trans: δ =0.88 (3H, d, J =7.0 Hz, 4-Me), 0.92, 0.94 (each 3H, d, J =7.0 Hz, C_6D_6), 1.10 (6H, dt, J =7.0 and $J_{\text{H-P}}$ =4.1 Hz, EtO), 1.26 (1H, ddd, J_{gem} =13.2, J_{3-4} =10.3, and J_{3-2} =2.9 Hz, one of 3-H), 1.76 (1H, m, the other of 3-H), 2.51 (1H, m, 4-H), 2.5–2.7 (2H, m, 6- CH_2P), 3.17, 3.84 (each 1H, dd, J_{gem} =9.5 and J =7.0 Hz, *i*-BuO), 4.65 (1H, m, 5-H), and 4.92 (1H, t, J_{2-3} =2.9 Hz, 2-H); ^{13}C NMR (C_6D_6) cis: δ =16.59 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 19.50, 19.54 (each *i*-BuO), 21.58 (d, $J_{\text{C-P}}$ =2.9 Hz, 4-Me), 26.62 (d, $J_{\text{C-P}}$ =2.0 Hz, 4-C), 28.91 (*i*-BuO), 32.83 (d, $J_{\text{C-P}}$ =139.9 Hz, 6- CH_2P), 36.14 (3-C), 61.58 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 61.76 (d, $J_{\text{C-P}}$ =6.9 Hz, EtO), 75.66 (*i*-BuO), 100.52 (2-C), 105.94 (d, $J_{\text{C-P}}$ =9.8 Hz, 5-C), and 143.22 (d, $J_{\text{C-P}}$ =9.8 Hz, 6-C); trans: δ =16.59 (d, $J_{\text{C-P}}$ =5.9 Hz), 19.50, 19.54 (each *i*-BuO), 21.39 (d, $J_{\text{C-P}}$ =2.9 Hz, 4-Me), 22.66 (d, $J_{\text{C-P}}$ =2.0 Hz, 4-C), 28.91 (*i*-BuO), 32.83 (d, $J_{\text{C-P}}$ =140.9 Hz, 6- CH_2P), 35.15 (3-C), 61.58 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 61.76 (d, $J_{\text{C-P}}$ =6.9 Hz, EtO), 75.03 (*i*-BuO), 97.59 (2-C), 106.69 (d, $J_{\text{C-P}}$ =9.8 Hz, 5-C), and 142.18 (d, $J_{\text{C-P}}$ =9.8 Hz, 6-C).

2-Butoxy-6-[(diethoxyphosphoryl)methyl]-4-propyl-3,4-dihydro-2H-pyran (6e): A 35:65 mixture of cis and trans isomers (^{13}C NMR); Colorless liquid; IR (neat) 1670, 1250, 1120, 1055, 1020, and 965 cm^{-1} ; ^1H NMR (C_6D_6) cis: δ =0.82 (3H, t, J =7.3 Hz, *n*-Pr), 0.88 (3H, t, J =7.3 Hz, *n*-BuO), 1.11 (6H, br t, J =7.0 Hz, EtO), 1.2–1.6 (9H, m, *n*-BuO, *n*-Pr, and 3-H), 1.88 (1H, dddd, J_{gem} =13.2, J_{3-4} =6.0, J_{3-2} =2.2, and J_{3-5} =1.0 Hz, one of 3-H), 2.14 (1H, m, 4-H), 2.59 (1H, dd, J_{gem} =13.5 and $J_{\text{H-P}}$ =21.0 Hz, one of 6- CH_2P), 2.66 (1H, dd, J_{gem} =13.5 and $J_{\text{H-P}}$ =21.0 Hz, the other of 6- CH_2P), 3.44 (1H, dt, J_{gem} =9.5 and J =7.2 Hz, *n*-BuO), 4.0–4.1 (5H, m, *n*-BuO and EtO), 4.66 (1H, m, 3-H), and 4.88 (1H, dd, J_{2-3} =8.1 and 2.2 Hz, 2-H); trans: δ =0.82 (3H, t, J =7.3 Hz, *n*-Pr), 0.88 (3H, t, J =7.3 Hz, *n*-BuO), 1.10 (6H, br t, J =7.0 Hz, EtO), 1.8–1.9 (9H, m, *n*-BuO, *n*-Pr, and 3-H), 2.45 (1H, m, 4-H), 2.5–2.7 (2H, m, 6- CH_2P), 3.4–3.5 (1H, m, *n*-BuO), 3.9–4.1 (5H, m, *n*-BuO and EtO), 4.74 (1H, m, 5-H), and 4.97 (1H, dd, J_{2-3} =3.0 and 2.2 Hz, 2-H); ^{13}C NMR (C_6D_6) cis: δ =14.05 (*n*-BuO), 14.29 (*n*-Pr), 16.57 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 19.70 (*n*-BuO), 20.30, 31.68 (each *n*-Pr), 32.24 (*n*-BuO), 32.71 (d, $J_{\text{C-P}}$ =139.9 Hz, 6- CH_2P), 34.50 (3-C), 38.54 (d, $J_{\text{C-P}}$ =2.0 Hz, 4-C), 61.72 (d, $J_{\text{C-P}}$ =6.9 Hz, EtO), 68.68 (*n*-BuO), 100.63 (2-C), 104.53 (d, $J_{\text{C-P}}$ =9.8 Hz, 5-C), and 143.50 (d, $J_{\text{C-P}}$ =10.8 Hz, 6-C); trans: δ =14.07 (*n*-BuO), 14.37 (*n*-Pr), 16.60 (d, $J_{\text{C-P}}$ =5.9 Hz, EtO), 19.77 (*n*-BuO), 20.10, 27.44 (each *n*-Pr),

32.21 (*n*-BuO), 32.97 (d, $J_{C-P}=139.9$ Hz, 6-CH₂P), 33.30 (3-C), 38.52 (d, $J_{C-P}=2.9$ Hz, 4-C), 61.57 (d, $J_{C-P}=5.9$ Hz, EtO), 68.23 (*n*-BuO), 97.62 (2-C), 105.16 (d, $J_{C-P}=10.8$ Hz, 5-C), and 142.38 (d, $J_{C-P}=9.8$ Hz, 6-C); MS m/z (rel intensity, %) 348 (M^+ , 7), 246 (23), 231 (base peak), 221 (22), 136 (25), 123 (27), 108 (37), 58 (20), and 57 (33).

2-Butoxy-4-phenyl-6-[(diethoxyphosphoryl)methyl]-3,4-dihydro-2H-pyran (6f): A 23:77 mixture of *cis* and *trans* isomers (¹³C NMR); Colorless liquid; IR (neat) 1670, 1600, 1250, 1125, 1050, 1025, 960, 755, and 695 cm⁻¹; ¹H NMR (C₆D₆) *cis*: $\delta=0.87$ (3H, t, $J=7.3$ Hz, *n*-BuO), 1.14 (6H, dt, $J=7.0$ and $J_{H-P}=1.1$ Hz, EtO), 1.38 (2H, sex, $J=7.3$ Hz, *n*-BuO), 1.57 (2H, quint, $J=7.3$ Hz, *n*-BuO), 1.92 (1H, ddd, $J_{gem}=13.2$, $J_{3-4}=10.6$, and $J_{3-2}=9.2$ Hz, one of 3-H), 2.10 (1H, dddd, $J_{gem}=13.2$, $J_{3-4}=6.0$, $J_{3-2}=1.8$, and $J_{3-5}=1.0$ Hz, the other of 3-H), 2.5–2.8 (2H, m, 6-CH₂P), 3.3–3.5 (2H, m, 4-H and *n*-BuO), 3.9–4.1 (5H, m, EtO and *n*-BuO), 4.76 (1H, m, 5-H), 4.93 (1H, dd, $J_{2-3}=9.2$ and 1.8 Hz, 2-H), and 7.0–7.3 (5H, m, Ph); *trans*: $\delta=0.88$ (3H, t, $J=7.3$ Hz, *n*-BuO), 1.09 (6H, t, $J=7.0$ Hz, EtO), 1.38 (2H, sex, $J=7.3$, *n*-BuO), 1.57 (2H, quint, $J=7.3$ Hz, *n*-BuO), 1.73 (1H, ddd, $J_{gem}=13.2$, $J_{3-4}=10.6$, and $J_{3-2}=2.7$ Hz, one of 3-H), 2.0–2.2 (1H, m, the other of 3-H), 2.5–2.8 (2H, m, 6-CH₂P), 3.75 (2H, m, 4-H and *n*-BuO), 3.9–4.1 (5H, m, EtO and *n*-BuO), 4.88 (1H, m, 5-H), 4.93 (1H, t, $J_{2-3}=3.2$ Hz, 2-H), and 7.0–7.3 (5H, m, Ph); ¹³C NMR (C₆D₆) *cis*: $\delta=13.64$ (*n*-BuO), 16.16, 16.21 (each d, $J_{C-P}=5.9$ Hz, EtO), 19.24, 31.76 (each *n*-BuO), 32.32 (d, $J_{C-P}=139.9$ Hz, 6-CH₂P), 37.29 (3-C), 38.20 (d, $J_{C-P}=2.0$ Hz, 4-C), 61.32, 61.43 (each d, $J_{C-P}=6.9$ Hz, EtO), 68.28 (*n*-BuO), 100.27 (2-C), 103.32 (d, $J_{C-P}=9.8$ Hz, 5-C), 126.32, 127.28, 128.33 (each Ar), 144.87 (d, $J_{C-P}=10.8$ Hz, 6-C), and 145.29 (Ar); *trans*: $\delta=14.11$ (*n*-BuO), 16.53, 16.59 (each d, $J_{C-P}=5.9$ Hz, EtO), 19.73, 32.15 (each *n*-BuO), 32.94 (d, $J_{C-P}=139.9$ Hz, 6-CH₂P), 34.60 (d, $J_{C-P}=2.0$ Hz, 4-C), 36.26 (3-C), 61.59, 61.86 (each d, $J_{C-P}=6.9$ Hz, EtO), 68.38 (*n*-BuO), 97.30 (2-C), 103.97 (d, $J_{C-P}=9.8$ Hz, 5-C), 126.66, 127.97, 128.79 (each Ar), 143.75 (d, $J_{C-P}=10.8$ Hz, 6-C), and 145.92 (Ar); MS m/z (rel intensity, %) 382 (M^+ , 2), 170 (32), 144 (23), 131 (21), 129 (34), 128 (36), 123 (34), 116 (31), 110 (21), 103 (23), 81 (26), 77 (21), and 30 (base peak).

2-Butoxy-4-(*p*-methoxyphenyl)-6-[(diethoxyphosphoryl)methyl]-3,4-dihydro-2H-pyran (6g): A 26:74 mixture of *cis* and *trans* isomers (¹³C NMR); Colorless liquid; IR (neat) 1675, 1610, 1510, 1460, 1445, 1370, 1250, 1030, 960, and 830 cm⁻¹; ¹H NMR (C₆D₆) *cis*: $\delta=0.87$ (3H, t, $J=7.3$ Hz, *n*-BuO), 1.11 (6H, dt, $J=7.0$ and $J_{H-P}=1.8$ Hz, EtO), 1.36 (2H, sex, $J=7.3$ Hz, *n*-BuO), 1.56 (2H, quint, $J=7.3$ Hz, *n*-BuO), 1.94 (1H, ddd, $J_{gem}=13.2$, $J_{3-4}=10.6$, and $J_{3-2}=9.2$ Hz one of 3-H), 2.13 (1H, ddd, $J_{gem}=13.2$, $J_{3-4}=6.0$, and $J_{3-2}=1.8$ Hz, the other of 3-H), 2.62, 2.71 (each 1H, dd, $J_{gem}=13.5$ and $J_{H-P}=21.6$ Hz, 6-CH₂P), 3.35 (3H, s, *p*-MeO), 3.45, 4.03 (each 1H, dt, $J_{gem}=9.5$ and $J=7.3$ Hz, *n*-BuO), 3.4–3.5 (1H, m, 4-H), 4.02 (4H, dq, $J=7.0$ and $J_{H-P}=8.1$ Hz, EtO), 4.80 (1H, m, 5-H), 4.95 (1H, dd, $J_{2-3}=9.2$ and 1.8 Hz, 2-H), 6.81, and 7.14 (each 2H, dt, $J=8.4$ and 1.8 Hz, Ar); *trans*: $\delta=0.89$ (3H, t, $J=7.3$ Hz, *n*-BuO), 1.11 (6H, dt, $J=7.0$ and $J_{H-P}=1.8$ Hz, EtO), 1.36 (2H, sex, $J=7.3$ Hz, *n*-BuO), 1.59 (2H, quint, $J=7.3$ Hz, *n*-BuO), 1.76 (1H, ddd, $J_{gem}=13.2$, $J_{3-4}=10.6$, and $J_{3-2}=3.2$ Hz, one of 3-H), 2.0–2.2 (1H, m, the other of 3-H), 2.5–2.8 (2H, m, 6-CH₂P), 3.4–4.5 (2H, m, 4-H and *n*-BuO), 3.78 (3H, s, *p*-MeO), 4.0–4.1 (5H, m, *n*-BuO, and EtO), 4.92 (1H, m, 5-H), 4.95 (1H, t, $J_{2-3}=3.2$ Hz, 2-H), 6.81, and 7.14 (each 2H,

dt, $J=8.4$ and 1.8 Hz, Ar); ¹³C NMR (C₆D₆) *cis*: $\delta=14.04$ (*n*-BuO), 16.56, 16.59 (each d, $J_{C-P}=5.9$ Hz, EtO), 19.65, 32.18 (each *n*-BuO), 32.73 (d, $J_{C-P}=138.9$ Hz, 6-CH₂P), 37.88 (d, $J_{C-P}=2.0$ Hz, 4-C), 38.01 (3-C), 54.83 (*p*-MeO), 61.65, 61.82 (each d, $J_{C-P}=6.9$ Hz, EtO), 68.69 (*n*-BuO), 100.77 (2-C), 104.19 (d, $J_{C-P}=10.8$ Hz, 5-C), 114.27, 128.58 (each Ar), 137.20 (d, $J_{C-P}=2.0$ Hz, Ar), 145.07 (d, $J_{C-P}=10.8$ Hz, 6-C), and 158.93 (Ar); *trans*: $\delta=14.11$ (*n*-BuO), 16.56, 16.62 (each d, $J_{C-P}=5.9$ Hz, EtO), 19.74, 32.20 (each *n*-BuO), 32.99 (d, $J_{C-P}=139.9$ Hz, 6-CH₂P), 33.89 (d, $J_{C-P}=2.0$ Hz, 4-C), 36.54 (3-C), 54.83 (*p*-MeO), 61.52, 61.76 (each d, $J_{C-P}=5.9$ Hz, EtO), 68.38 (*n*-BuO), 97.42 (2-C), 104.37 (d, $J_{C-P}=9.8$ Hz, 5-C), 114.34, 128.58 (each Ar), 137.89 (d, $J_{C-P}=2.0$ Hz, Ar), 143.66 (d, $J_{C-P}=10.8$ Hz, 6-C), and 158.93 (Ar); MS m/z (rel intensity, %) 412 (M^+ , 8), 312 (34), 231 (88), 200 (36), 174 (28), 161 (41), 136 (21), 123 (27), 69 (54), and 30 (base peak).

2-Butoxy-4,4-dimethyl-6-[(diethoxyphosphoryl)methyl]-3,4-dihydro-2H-pyran (6h): Colorless liquid; IR (neat) 1670, 1645, 1465, 1445, 1390, 1365, 1250, 1160, 1120, 1055, 1025, 960, and 795 cm⁻¹; ¹H NMR (C₆D₆) $\delta=0.85$ (3H, t, $J=7.0$ Hz, *n*-BuO), 0.95, 1.03 (each 3H, s, 4-Me), 1.11 (6H, dt, $J=7.0$ and $J_{H-P}=1.4$ Hz, EtO), 1.2–1.8 (6H, m, *n*-BuO and 3-H), 2.56, 2.64 (each 1H, dd, $J_{gem}=12.0$ and $J_{H-P}=20.0$ Hz, 6-CH₂P), 3.43 (1H, dt, $J_{gem}=9.5$ and $J=6.6$ Hz, *n*-BuO), 4.02 (4H, dq, $J=7.0$ and $J_{H-P}=8.1$ Hz, EtO), 4.05 (1H, dt, $J_{gem}=9.5$ and $J=6.6$ Hz, *n*-BuO), 4.54 (1H, d, $J_{H-P}=4.4$ Hz, 5-H), and 4.94 (1H, dd, $J_{2-3}=7.0$ and 3.0 Hz, 2-H); ¹³C NMR (C₆D₆) $\delta=14.07$ (*n*-BuO), 16.59 (d, $J_{C-P}=5.9$ Hz, EtO), 19.71 (*n*-BuO), 29.88 (d, $J_{C-P}=2.0$ Hz, 4-C), 30.36 (d, $J_{C-P}=2.9$ Hz, 4-Me), 31.55 (d, $J_{C-P}=3.9$ Hz, 4-Me), 32.25 (*n*-BuO), 32.73 (d, $J_{C-P}=139.9$ Hz, 6-CH₂P), 41.83 (3-C), 61.63 (d, $J_{C-P}=5.9$ Hz, EtO), 68.78 (*n*-BuO), 98.93 (2-C), 110.64 (d, $J_{C-P}=10.8$ Hz, 5-C), and 141.79 (d, $J_{C-P}=10.8$ Hz, 6-C); MS m/z (rel intensity, %) 334 (M^+ , 14), 245 (base peak), 235 (54), 123 (19), and 41 (23).

General Procedure for the Hydrolysis and Cyclization Sequence of 6a–h Leading to 2-Cyclohexen-1-ones 7a–f.

As a typical procedure the conversion of 6a into 7a is described as follows: To a solution of 6a (0.055 g, 0.198 mmol) in THF (4 ml) was added 4 M hydrochloric acid (2 ml). After stirring at room temperature for 5 min, the mixture was extracted with dichloromethane (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using ethyl acetate–methanol (9:1 v/v) to give 7a (0.04 g, 87%). Other compounds 6b–h were similarly treated under the reaction conditions listed in Table 2. The purification of 7b–f was carried out by silica-gel column chromatography using ethyl acetate–methanol: 7b, 7c, and 7e: 9:1 v/v; 7d: 98:2 v/v; 7f: 19:1 v/v.

2-(Diethoxyphosphoryl)-2-cyclohexen-1-one (7a): Colorless liquid; IR (neat) 1675, 1600, 1345, 1245, 1160, 1060, 1025, and 965 cm⁻¹; ¹H NMR (CDCl₃) $\delta=1.33$ (6H, dt, $J=7.0$ and $J_{H-P}=0.8$ Hz, EtO), 2.06 (2H, quint, $J_{5-4}=J_{5-6}=6.6$ Hz, 5-H), 2.50 (2H, t, $J_{6-5}=6.6$ Hz, 6-H), 2.54 (2H, dt, $J_{4-5}=6.6$ and $J_{4-3}=4.1$ Hz, 4-H), 4.17 (4H, m, EtO), and 7.92 (1H, dt, $J_{3-4}=4.1$ and $J_{H-P}=21.3$ Hz, 3-H); ¹³C NMR (CDCl₃) $\delta=16.39$ (d, $J_{C-P}=5.9$ Hz, EtO), 22.03 (5-C), 26.82 (d, $J_{C-P}=14.7$ Hz, 4-C), 38.48 (d, $J_{C-P}=7.8$ Hz, 6-C), 62.48 (d, $J_{C-P}=5.9$ Hz, EtO), 131.60 (d, $J_{C-P}=181.9$ Hz, 2-C), 163.37 (d, $J_{C-P}=5.9$ Hz, 3-C), and 196.05 (d, $J_{C-P}=5.9$ Hz, 1-C); MS m/z (rel intensity, %) 232 (M^+ , 48), 204 (37), 177 (20), 176 (94), 159 (46), 149 (48), 148 (76), 132 (21), 127 (22), 123, (26), 121 (78), 120 (52), 106 (49), 95

(30), 94 (30), 91 (21), 81 (47), and 79 (26). HRMS Found: m/z 232.0859. Calcd for $C_{10}H_{17}O_4P$: M, 232.0863.

2-(Diethoxyphosphoryl)-5-methyl-2-cyclohexen-1-one (7b): Colorless liquid; IR (neat) 1675, 1600, 1360, 1340, 1240, 1155, 1095, 1050, 1020, 960, 790, 750, and 620 cm^{-1} ; 1H NMR ($CDCl_3$) δ =1.09 (3H, d, J =5.9 Hz, 5-Me), 1.32 (6H, dt, J =7.0 and J_{H-P} =0.7 Hz, EtO), 2.1–2.4 (3H, m, 4- and 5-H), 2.59 (2H, m, 6-H), 4.16 (4H, m, EtO), and 7.88 (1H, ddd, J_{3-4} =7.7, 2.2, and J_{H-P} =20.5 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ =16.37 (d, J_{C-P} =5.9 Hz, EtO), 20.59 (5-Me), 29.70 (5-C), 34.98 (d, J_{C-P} =14.7 Hz, 4-C), 46.58 (d, J_{C-P} =7.8 Hz, 6-C), 62.42, 62.46 (each d, J_{C-P} =5.9 Hz, EtO), 131.28 (d, J_{C-P} =182.9 Hz, 2-C), 162.69 (d, J_{C-P} =5.9 Hz, 3-C), and 196.29 (d, J_{C-P} =5.9 Hz, 1-C); MS m/z (rel intensity, %) 246 (M^+ , 50), 231 (27), 203 (26), 176 (39), 175 (21), 173 (21), 149 (35), 148 (41), 121 (45), 120 (34), 91 (26), 81 (27), 79 (27), and 29 (base peak). HRMS Found: m/z 246.1065. Calcd for $C_{11}H_{19}O_4P$: M, 246.1019.

2-(Diethoxyphosphoryl)-5-propyl-2-cyclohexen-1-one (7c): Colorless liquid; IR (neat) 1675, 1600, 1345, 1240, 1050, 1025, 970, 790, and 755 cm^{-1} ; 1H NMR ($CDCl_3$) δ =0.87 (3H, t, J =6.2 Hz, n -Pr), 1.2–1.5 (4H, m, n -Pr), 1.27 (6H, dt, J =7.0 and J_{H-P} =0.7 Hz, EtO), 2.1–2.4 (3H, m, 4- and 5-H), 2.56 (2H, m, 6-H), 4.12 (4H, m, EtO), and 7.84 (1H, ddd, J_{3-4} =5.5, 2.2, and J_{H-P} =21.1 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ =13.98 (n -Pr), 16.37 (d, J_{C-P} =5.9 Hz, EtO), 19.50 (n -Pr), 33.31 (d, J_{C-P} =14.7 Hz, 4-C), 34.27, 37.72 (each n -Pr), 44.87 (d, J_{C-P} =7.8 Hz, 6-C), 62.45 (d, J_{C-P} =4.9 Hz, EtO), 131.41 (d, J_{C-P} =182.9 Hz, 2-C), 162.83 (d, J_{C-P} =5.9 Hz, 3-C), and 196.42 (d, J_{C-P} =5.9 Hz, 1-C); MS m/z (rel intensity, %) 274 (M^+ , 3), 222 (base peak), 195 (32), 194 (37), 179 (23), 167 (24), 152 (24), 151 (20), 139 (33), 125 (35), 123 (44), 121 (25), 109 (23), 97 (30), and 81 (35). HRMS Found: m/z 274.1423. Calcd for $C_{13}H_{23}O_4P$: M, 274.1333.

2-(Diethoxyphosphoryl)-5-phenyl-2-cyclohexen-1-one (7d): Colorless liquid; IR (neat) 1680, 1600, 1500, 1450, 1390, 1365, 1345, 1250, 1215, 1100, 1060, 1025, 970, 790, 760, and 700 cm^{-1} ; 1H NMR ($CDCl_3$) δ =1.34 (6H, dt, J =7.0 and J_{H-P} =4.8 Hz, EtO), 2.6–2.9 (4H, m, 4- and 6-H), 3.37 (2H, m, 5-H), 4.20 (4H, m, EtO), 7.2–7.4 (5H, m, Ph), and 7.96 (1H, ddd, J_{3-4} =5.5, 2.6, and J_{H-P} =19.5 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ =16.39 (d, J_{C-P} =4.9 Hz, EtO), 34.58 (d, J_{C-P} =14.7 Hz, 4-C), 40.14 (5-C), 45.27 (d, J_{H-P} =7.8 Hz, 6-C), 62.54, 62.56 (each d, J_{C-P} =5.9 Hz, EtO), 126.59, 127.25, 128.89 (each Ph), 131.59 (d, J_{C-P} =18.4 Hz, 2-C), 142.23 (Ph), 162.18 (d, J_{C-P} =5.9 Hz, 3-C), and 195.57 (d, J_{C-P} =5.9 Hz, 1-C); MS m/z (rel intensity, %) 308 (M^+ , 7), 228 (82), 200 (51), 184 (22), 183 (base peak), 182 (29), 155 (31), and 67 (23). HRMS Found: m/z 308.1172. Calcd for $C_{16}H_{21}O_4P$: M, 308.1176.

2-(Diethoxyphosphoryl)-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one (7e): Colorless liquid; IR (neat) 1675, 1610, 1510, 1250, 1180, 1060, 1025, 970, 835, 795, and 750 cm^{-1} ; 1H NMR ($CDCl_3$) δ =1.35 (6H, dt, J =7.3 and J_{H-P} =4.4 Hz, EtO), 2.5–2.9 (4H, m, 4- and 6-H), 3.30 (1H, m, 5-H), 3.80 (3H, s, *p*-MeO), 4.19 (4H, m, EtO), 6.88 (2H, dt, J =8.8 and 2.2 Hz, Ar), 7.15 (2H, dt, J =8.8 and 2.2 Hz, Ar), and 7.95 (1H, ddd, J_{3-4} =5.5, 2.2, and J_{H-P} =20.2 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ =16.40 (d, J_{C-P} =5.9 Hz, EtO), 34.88 (d, J_{C-P} =14.7 Hz, 4-C), 39.44 (5-C), 45.61 (d, J_{C-P} =7.9 Hz, 6-C), 55.30 (*p*-MeO), 62.53, 62.58 (each d, J_{C-P} =5.9 Hz, EtO), 114.24, 127.57 (each Ar), 131.55 (d, J_{C-P} =182.9 Hz, 2-C), 134.41, 158.71 (each Ar), 162.33 (d, J_{C-P} =5.9 Hz, 3-C), and 195.57 (d, J_{C-P} =5.9 Hz, 1-C); MS m/z (rel intensity, %) 338 (M^+ , 79), 337 (21), 217 (27), 201 (28), 200

(45), 172 (22), 134 (base peak), 128 (26), 121 (54), 119 (30), 115 (28), 91 (37), 81 (34), and 77 (29). HRMS Found: m/z 338.1284. Calcd for $C_{17}H_{23}O_5P$: M, 338.1282.

2-(Diethoxyphosphoryl)-5,5-dimethyl-2-cyclohexen-1-one (7f): Colorless liquid; IR (neat) 1675, 1600, 1385, 1350, 1235, 1050, 1020, 965, 780, and 750 cm^{-1} ; 1H NMR ($CDCl_3$) δ =1.06 (6H, s, 5-Me), 1.32 (6H, t, J =7.0 Hz, EtO), 2.35 (2H, d, J_{H-P} =1.1 Hz, 6-H), 2.42 (1H, t, J_{4-3} = J_{H-P} =4.0 Hz, 4-H), 4.16 (4H, m, EtO), and 7.81 (1H, dt, J_{3-4} =4.0 and J_{H-P} =20.5 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ =16.37 (d, J_{C-P} =5.9 Hz, EtO), 28.13 (5-Me), 33.74 (5-C), 40.91 (d, J_{C-P} =15.7 Hz, 4-C), 52.14 (d, J_{C-P} =7.8 Hz, 6-C), 62.45 (d, J_{C-P} =5.9 Hz, EtO), 130.56 (d, J_{C-P} =182.9 Hz, 2-C), 161.66 (d, J_{C-P} =5.9 Hz, 3-C), and 196.26 (d, J_{C-P} =5.9 Hz, 1-C). MS m/z (rel intensity, %) 260 (M^+ , 3), 176 (12), 149 (14), 121 (18), 81 (27), 79 (20), and 30 (base peak). HRMS Found: m/z 260.1179. Calcd for $C_{12}H_{21}O_4P$: M, 260.1176.

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