2456 © 1992 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***65***, *2456—2464 (1992)* [Vol. 65, No. 9

A New Annulation Reagent, 2-Oxo-3-alkenylphosphonates. Reactions with Carbonyl-Stabilized Carbanions or Silyl Enol Ethers Leading to Cyclohexenones

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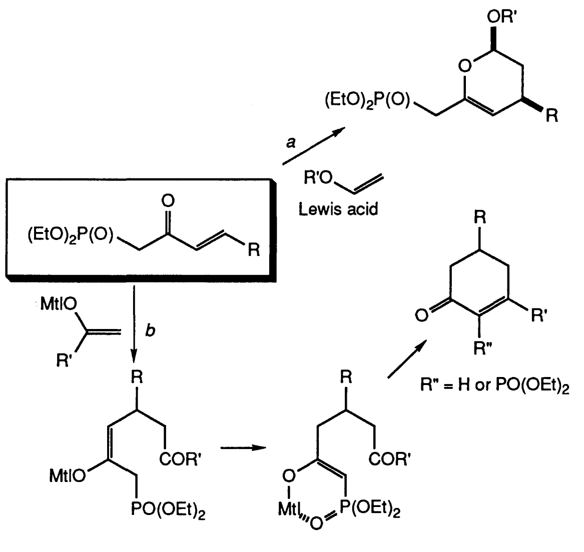
(Received January 18, 1992)

The reactions of 2-oxo-3-alkenylphosphonates with carbonyl-stabilized carbanions directly lead to 2-cyclohexen-1-ones through a sequence of Michael reaction and intramolecular Horner–Emmons olefination. On the other hand, the Lewis acid-mediated reactions with silyl enol ethers produce 1,5-diketones as Michael adducts, which then undergo cyclization on treatment with sodium hydride or triethylamine/zinc (II) bromide to afford 2-cyclohexen-1-ones or 2-phosphinyl-2-cyclohexen-1-ones, respectively.

2-Oxo-3-alkenylphosphonates as phosphorus-functionalized enones are readily synthesized by the reactions of diethyl 2-oxopropylphosphonate with aldehydes.[1] They have been utilized as heterodienes in the inverse electron-demand Diels–Alder reactions with vinyl ethers under the influence of a Lewis acid to lead to *cis*-3,4-dihydro-2*H*-pyrans as the major stereoisomeric cycloadducts (Route *a* in Scheme 1);[2] these hetero Diels–Alder reactions have found some synthetic applications as shown in the synthesis of 5-substituted 2-phosphinyl-2-cyclohexen-1-ones[1] and functionalized 2-chromanones.[3]



Scheme 1.

In connection with our study on synthetic utilization of 2-oxo-3-alkenylphosphonates as new synthetic reagents, our interest in their use as Michael acceptors[1] led us to investigate their synthetic applications to a modified Robinson annulation method based on the sequential Michael reaction and Horner–Emmons olefination.

The Robinson annulation, the base-catalyzed Michael addition of ketones to methyl vinyl ketone followed by the intramolecular aldol condensation producing cyclohexenones, is a classical but still widely utilized ring construction methodology in organic synthesis.[4] A variety of improvements for the classical Robinson annulation reaction have been studied with respect to the modification of acceptors[5] and enolates[6–8] and the development of milder reaction conditions.[6–13] The final step of cyclohexenone formation by intramolecular aldol condensation of the intermediary 1,5-diketones has a critical problem of poor regioselectivity.[14] This problem was partly solved by use of (2-ethoxy-1,3-pentadienyl)triphenylphosphonium iodide as modified acceptor. Therein, the initial Michael reaction is followed by an intramolecular Wittig reaction.[15] However, the lithium enolates employed showed only limited reactivity, and the phosphonium salts are not readily available.

We now wish to describe here a general procedure for the modified cyclohexenone annulation method: The Michael reaction of the readily available 2-oxo-3-alkenylphosphonates is followed by the intramolecular Horner–Emmons olefination of the resulting phosphorus-stabilized enolates. In addition, the cyclohexenone annulation reaction leading to 2-phosphinyl-2-cyclohexen-1-one derivatives has been demonstrated. It consists of the Michael reaction of 2-oxo-3-alkenylphosphonates and subsequent intramolecular Knoevenagel condensation (Route *b* in Scheme 1). Facile and effective synthesis of diethyl 2-oxo-3-butenylphosphonate is also presented.

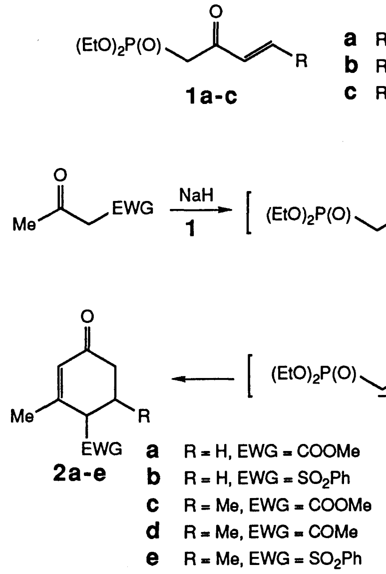
Results and Discussion

The Annulation Reaction of Diethyl 2-Oxo-3-alkenylphosphonates 1a, b with Carbonyl-Stabilized Carbanions. First of all, carbonyl-stabilized carbanions were employed as Michael donors for the cyclohexenone annulation reaction of enones **1**. The reactions of **1** with carbonyl-stabilized carbanions, such as those derived from methyl 3-oxobutanoate, 2,4-pentanedione, and 1-(phenylsulfonyl)-2-propanone by treatment with sodium

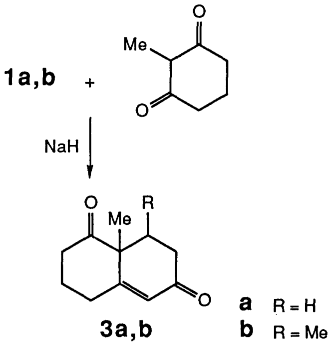
Table 1. Reaction of 2-Oxo-3-alkenylphosphonates **1** with Carbonyl-Stabilized Carbanions

Entry	Enone	Donor	Reaction conditions[a]		Product	Yield[b]/%
			Temp/°C	Time/h		
1	**1a**	Methyl 3-oxobutanoate	−40	2	**2a**	41
2	**1a**	1-(Phenylsulfonyl)-2-propanone	0[c]	6	**2b**	52
3	**1b**	Methyl 3-oxobutanoate	0	2	**2c**	71 4:1[d]
4	**1b**	2,4-Pentanedione	0	2	**2d**	48 4:1[d]
5	**1b**	1-(Phenylsulfonyl)-2-propanone	R.T.[c]	24	**2e**	68 Single[e]
6	**1a**	2-Methyl-1,3-cyclohexanedione	Reflux	16	**3a**	48
7	**1b**	2-Methyl-1,3-cyclohexanedione	Reflux	16	**3b**	47 8:7[d]

a) Unless otherwise mentioned, all reactions were carried out in THF under nitrogen in the presence of sodium hydride (1.1 equiv). b) Yield of isolated products. c) Prior to the Michael reaction, the anion generation was conducted at room temperature for 30 min. d) Obtained as an inseparable mixture of two stereoisomers whose ratio was based on the ^{1}H NMR spectrum of the crude reaction mixture. e) Based on the ^{1}H NMR spectrum of the crude product.



Scheme 2.



Scheme 3.

hydride, were carried out to give cyclohexenone derivatives **2** in moderate yields (Scheme 2 and Table 1). These reactions consist of the initial Michael reactions, the proton migration forming the phosphonyl-stabilized anions **A**, and the subsequent intramolecular Horner–Emmons olefinations.

Two stereoisomers were formed in the reactions of 2-oxo-3-pentenylphosphonate **1b** (Entries 3 and 4); the isomer ratios were not satisfactorily high (4:1). Only the reaction with the sulfonyl-substituted methyl ketone produced **2e** as the sole stereoisomer. The stereostructure of **2e** was assigned to be 4,5-*trans* on the basis of the NOE spectrum, in which notable signal enhancement was observed between the ortho two protons of the 4-phenylsulfonyl substituent and H-5 (Entry 5).

Enones **1a** and **1b** produced the corresponding ring-fused cyclohexenone derivatives **3a** and **3b** in moderate yields on treatment with the cyclic stabilized carbanion derived from 2-methyl-1,3-cyclohexanedione, while the stereoselectivity of **3b** was again far from a satisfactory level (Scheme 3 and Entries 6 and 7).

On the other hand, the lithium enolate of acetone (2 equiv) gave no condensation product in the reaction with enone **1b**, but 4-hydroxy-4-methyl-2-pentanone was produced as the self aldol adduct of acetone in 55% yield. Use of one equivalent of the lithium enolate of acetone resulted in the quantitative recovery of the starting enone **1b**.

Thus, one of the critical problems in the Michael reactions of **1** under basic conditions is that enones **1** have two highly acidic protons, which are prone to be readily abstracted by the anionic donors employed. Therefore, only the Michael donors derived from active methylene compounds such as β-keto esters, β-diketones, and α-sulfonyl ketones can be successfully employed, where the simple one-pot cyclohexenone annulation reaction takes place under basic reaction conditions. This serious limitation was circumvented by performing the Lewis acid-catalyzed Michael reactions of silyl enol ethers as Michael donors.

Cyclohexenone Annulation through the Michael Reactions of Enones 1 with Silyl Enol Ethers Followed by the Intramolecular Horner–Emmons Olefinations or Knoevenagel Condensations. Lewis acid-catalyzed reaction of silyl enol ethers with α,β-unsaturated carbonyl compounds affording 1,5-dicarbonyl compounds, known as Mukaiyama reaction,[7] has been

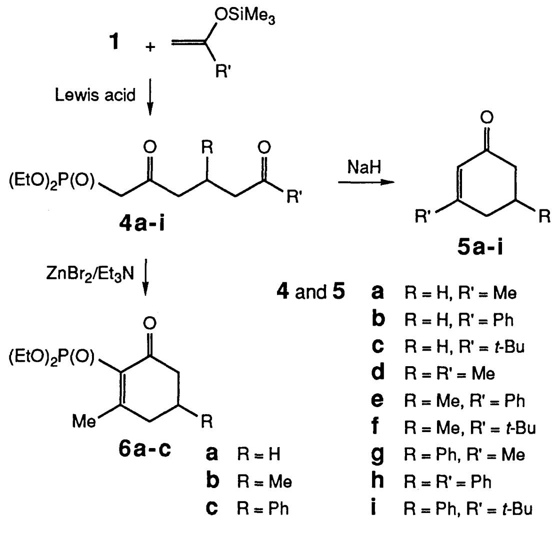
Table 2. Reactions of 2-Oxo-3-alkenylphosphonates **1** with Silyl Enol Ethers Followed by Cyclization

Entry	Enone	Donor[a] R′	Reaction conditions[b] Additive[e]	Temp/°C	Time/h	Product (yield/%)[c]	Reaction conditions[d] Additive[f]	Temp/°C	Time/h	Solvent[g]	Product (yield/%)[c]
1	**1a**	Me	A	−78	9	**4a**[h]	C	R.T.	2	THF	**5a** (54)[i]
2	**1a**	Ph	A	−50	16	**4b** (86)	C	R.T.	2	THF	**5b** (95)
3	**1a**	*t*-Bu	A	−50	18	**4c** (85)	C	Reflux	2	THF[j]	**5c** (74)
4	**1b**	Me	A	−50	18	**4d**[h]	C	R.T.	2	THF	**5d** (52)[i]
5	**1b**	Ph	A	−78	2	**4e** (78)	C	R.T.	2	THF	**5e** (54)[i]
6	**1b**	*t*-Bu	A	−50	16	**4f** (78)	C	Reflux	3	THF[j]	**5f** (85)
7	**1b**	*t*-Bu	B	−50	18	**4f** (65)					
8	**1c**	Me	B	−50	18	**4g**[h]	C	R.T.	2	THF	**5g** (48)[i]
9	**1c**	Ph	B	−50	18	**4h**[h]	C	R.T.	2	THF	**5h** (52)[i]
10	**1c**	*t*-Bu	B	−50	18	**4i** (74)	C	Reflux	2	THF[j]	**5i** (94)
11	**1a**	Me	A	−78	9	**4a**[h]	D	R.T.	24	DCM	**6a** (72)[i]
12	**1b**	Me	A	−50	18	**4d**[h]	D	R.T.	24	DCM	**6b** (77)[i]
13	**1c**	Me	B	−50	18	**4g**[h]	D	R.T.	24	DCM	**6c** (78)[i]
14	**1a**	$n=0$[k]	B	−50	18	**7a**[h]	C	R.T.	2	THF	**8a** (28)[i]
15	**1c**	$n=0$[k]	B	−50	18	**7b**[h]	C	R.T.	3.5	THF	**8b** (48)[i] Single[l]
16	**1a**	$n=1$[m]	B	−50	18	**7c**[h]	C	R.T.	2	THF	**8c** (52)[i]
17	**1b**	$n=1$[m]	B	−50	18	**7d**[h]	C	R.T.	2	THF	**8d** (52)[i] 4:1[l]
18	**1c**	$n=1$[m]	B	−50	18	**7e**[h]	C	R.T.	3.5	THF	**8e** (58)[i] 4:1[l]

a) Donor molecules employed were either 1-substituted 1-(trimethylsilyloxy)ethenes or 1-(trimethylsilyloxy)cycloalkenes, where R′ denotes substituent in ethenes or the number of ring carbons minus 5. See footnote k) and m). b) Reaction conditions for the Michael additions which were carried out in dichloromethane. c) Yield of isolated product. d) Reaction conditions for the cyclization of the Michael adducts. e) A: $TiCl_4/Ti(i\text{-}PrO)_4$ (1 equiv/0.2 equiv). B: $TiCl_4$ (1.1 equiv). f) C: NaH (1.2 equiv). D: $ZnBr_2/Et_3N$ (1.2 equiv/1.2 equiv). g) THF: tetrahydrofuran. DCM: dichloromethane. h) Yield was measured after its conversion to **5**. i) Yield based on enones **1**. j) A mixture of THF and hexamethylphosphoric triamide (HMPA) was used (THF/HMPA=3:1 v/v). k) 1-(Trimethylsilyloxy)cyclopentene (see Scheme 5). l) Based on the ^{13}C NMR spectrum of the crude product. m) 1-(Trimethylsilyloxy)cyclohexene (see Scheme 5).

extensively explored as an alternative to the classical Robinson annulation sequence. This methodology may be more successfully applied to the cyclohexenone annulation using the base-sensitive enones **1** since the Mukaiyama procedure can be carried out under acidic conditions.

The trimethylsilyl enol ethers derived from both acyclic and cyclic ketones, such as 2-(trimethylsilyloxy)propene, 3,3-dimethyl-2-(trimethylsilyloxy)-1-butene, 1-phenyl-1-(trimethylsilyloxy)ethene, 1-(trimethylsilyloxy)cyclopentene, and 1-(trimethylsilyloxy)cyclohexene, were used as Michael donors. These trimethylsilyl enol ethers were easily synthesized by the standard procedure.[16)]



Scheme 4.

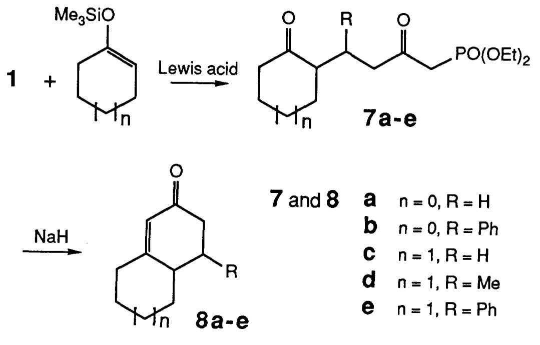
Results of the Michael reactions of enones **1** with acyclic silyl enol ethers and the cyclohexenone cyclization of the resulting 1,5-diketones **4** are summarized in Scheme 4 and Table 2.

The Michael reactions of enone **1b** with 3,3-dimethyl-2-(trimethylsilyloxy)-1-butene affording 1,5-diketone **4f** were successfully catalyzed by using $TiCl_4$ or a mixture of $TiCl_4$ (1 equiv) and Ti(*i*-PrO)$_4$ (0.2 equiv) at a low temperature (−50 °C) (Entries 6 and 7). Similar Michael reactions of other enones **1** with acyclic silyl enol ethers were carried out by employing either of the titanium catalysts to give the corresponding 1,5-diketones **4** in good yields (Entries 1—5 and 8—10).

1,5-Diketones **4b**, **c**, **e**, **f**, **i** as the Michael adducts could be purified by silica-gel column chromatography, and were then successfully cyclized to the corresponding cyclohexenones **5b**, **c**, **e**, **f**, **i**, respectively, on treatment with sodium hydride in dry THF (Entries 2, 3, 5, 6, and 10). Although the other 1,5-diketones **4a**, **d**, **g**, **h** were unstable under the purification procedure by silica-gel column chromatography, they underwent smooth cyclization without further purification to give the corresponding cyclohexenones **5a**, **d**, **g**, **h**, respectively, under similar conditions (Entries 1, 4, 8, and 9).

Crude 1,5-diketones **4a**, **d**, **g** were transformed to the corresponding 3-methyl-2-phosphinyl-2-cyclohexen-1-ones **6a**, **b**, **c**, respectively, by the intramolecular Knoevenagel condensation[17,18)] which was performed in the presence of $Et_3N/ZnBr_2$ in dry CH_2Cl_2 at room temperature (Entries 11—13). This two-step reaction sequence starting from enones **1** to give 2-phosphinyl-substituted cyclohexenone derivatives **6** proceeds in good yields.

Michael reactions of enones **1** with cyclic silyl enol ethers in the presence of $TiCl_4$ afforded unstable 1,5-diketones **7** as the Michael adducts, which were then cyclized without further purification to the corresponding ring-fused cyclohexenones **8** in moderate yields on treatment with sodium hydride (Scheme 5 and Entries 14—18). Stereoselectivity of the ring-fused cyclohexenones **8** was far from a satisfactory level (4 : 1) except for **8b** (single isomer).



Scheme 5.

In conclusion, a modified cyclohexenone annulation reaction employing 2-oxo-3-alkenylphosphonates **1** has been developed, which is based on the Michael reaction and intramolecular Horner–Emmons olefination. This overall reaction sequence, synthetically equivalent to the ordinary Robinson annulation, provides cyclohexenones in the yields comparable to those obtained by other methods. In addition, a facile and effective reaction leading to the 2-phosphinyl-2-cyclohexen-1-ones bearing substituents at 3-, 5-positions has been presented. We believe that **1** is one of the most promising annulation reagent for the regioselective synthesis of substituted cyclohexenones.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with JASCO IRA-1 and A-702 spectrometers. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-100 (100 MHz for ^1H NMR and 25.05 MHz for ^{13}C NMR) and GSX-270 (270 MHz for ^1H NMR and 67.94 MHz for ^{13}C NMR) instruments. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra and high-resolution mass spectra

(HRMS) were measured with a JEOL-01SG-2 spectrometer at an ionization energy of 70 eV. Elemental analyses were performed on a Hitachi 026 CHN analyzer. For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silica gel 60 (Merck) were employed. Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus.

Materials. 2-Oxo-3-alkenylphosphonates **1a**—**c** are all known compounds and were prepared according to the reported methods.[1] The improved synthetic method of the parent enone **1a** is described below. 1-(Phenylsulfonyl)-2-propanone was synthesized in 96% yield by the literature procedure.[19] The following silyl enol ethers were also synthesized by the literature procedures:[16] 2-(trimethylsilyloxy)propene (73% yield), 3,3-dimethyl-2-(trimethylsilyloxy)-1-butene (94% yield), 1-phenyl-1-(trimethylsilyloxy)ethene (90% yield), 1-(trimethylsilyloxy)cyclopentene (94% yield), and 1-(trimethylsilyloxy)cyclohexene (96% yield).

Diethyl 2-Oxo-3-butenylphosphonate (1a): In our previous procedure,[1] **1a** was prepared by oxidation of diethyl 2-oxo-4-(phenylthio)butylphosphonate with sodium periodate, followed by thermolysis at 145 °C under vacuum; the starting phosphonate was obtained in 58% yield by alkylation of the dianion of diethyl 2-oxopropylphosphonate. In the present work, the improved synthesis of diethyl 2-oxo-4-(phenylthio)butylphosphonate was investigated as shown below: Treatment of methyl 3-(phenylthio)propionate, prepared by the literature procedure,[20] with lithium diethyl methylphosphonate (2 equiv) in dry THF at −78 °C gave diethyl 2-oxo-4-(phenylthio)butylphosphonate quantitatively.

The Annulation Reaction of Diethyl 2-Oxo-3-alkenylphosphonates 1a, b with Carbonyl-Stabilized Carbanions Leading to Cyclohexenones 2 and 3. As a typical example, the synthesis of **2a** is described as follows: To a suspension of sodium hydride (60% in mineral oil, 0.044 g, 1.1 mmol) in dry THF (8 ml) was added methyl 3-oxobutanoate (0.116 g, 1 mmol) under nitrogen. After 30 min at room temperature, enone **1a** (0.206 g, 1 mmol) was added at −40 °C. The reaction mixture was stirred at −40 °C for 2 h and acidified with 1 M hydrochloric acid (1 M=1 mol dm^{-3}), followed by extraction with dichloromethane (30 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane–ethyl acetate (4 : 1 v/v)) to give **2a** (0.069 g, 41%).

Reaction conditions and yields of **2a**—**e** and **3a**, **b** are summarized in Table 1.

Methyl 2-Methyl-4-oxo-2-cyclohexene-1-carboxylate (2a). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (4 : 1 v/v)); IR (neat) 2980, 1730, 1660, 1440, 1350, 1200, 1160, and 1020 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ=2.02 (3H, br s, COOMe), 2.2—2.6 (4H, m, H-5 and H-6), 3.31 (1H, br t, $J_{1\text{-}6}$=4.9 Hz, H-1), 3.78 (3H, s, COOMe), and 5.96 (1H, br s, H-3); ^{13}C NMR (CDCl$_3$) δ=23.48 (2-Me), 26.08, 34.28 (C-5 and C-6), 45.90 (C-1), 52.40 (COOMe), 128.56 (C-3), 156.86 (C-2), 172.05 (COOMe), and 198.19 (C-4); MS *m/z* (rel intensity, %) 169 (M$^+$+1, 13), 168 (M$^+$, 99), 140 (83), 112 (base peak), 109 (87), and 108 (11). Found: C, 64.65; H, 7.18% (*m/z* 168.0785). Calcd for C$_9$H$_{12}$O$_3$: C, 64.27; H, 7.19% (M, 168.0786).

3-Methyl-4-phenylsulfonyl-2-cyclohexen-1-one (2b). Colorless solid (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); mp 107—108 °C (diethyl ether–hexane); IR (KBr) 1650, 1620, 1275, 1225, 1120, and 1070 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.15 (3H, br s, 3-Me), 2.2—2.8 (4H, m, H-5 and H-6), 3.88 (1H, dd, $J_{4\text{-}5}$=5.6 and 1.8 Hz, H-4), 6.15 (1H, br s, H-2), and 7.6—8.0 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=24.23 (3-Me), 24.81, 31.68 (C-5 and C-6), 65.20 (C-4), 128.66, 129.60, 132.45, 134.45, 138.12 (Ph and C-2), 150.30 (C-3), and 196.65 (C-1); MS *m/z* (rel intensity, %) 250 (M$^+$, 4), 125 (5), 110 (5), 109 (base peak), 108 (57), and 81 (5). Found: C, 62.00; H, 5.83% (*m/z* 250.0663). Calcd for C$_{13}$H$_{14}$O$_3$S: C, 62.38; H, 5.64% (M, 250.0663).

Methyl 2,6-Dimethyl-4-oxo-2-cyclohexene-1-carboxylate (2c). Colorless liquid (an inseparable 1 : 4 mixture of stereoisomers (^{1}H and ^{13}C NMR), silica-gel column chromatography using hexane–ethyl acetate (4 : 1 v/v)); IR (neat) 2980, 1730, 1660, 1630, 1440, 1350, 1200, and 1160 cm^{-1}; ^{1}H NMR (CDCl$_3$) minor isomer: δ=1.97 (3H, br s, 2-Me), 2.26 (1H, m, H-6), 3.23 (1H, d, $J_{1\text{-}6}$=5.1 Hz, H-1), and 3.74 (3H, s, COOMe). Other signals overlap with those of the major isomer: major isomer: δ=1.08 (3H, d, $J_{\text{Me-}6}$=6.6 Hz, 6-Me), 1.96 (3H, br s, 2-Me), 2.0—2.6 (3H, m, H-5 and H-6), 3.07 (1H, d, $J_{1\text{-}6}$=7.7 Hz, H-1), 3.78 (3H, s, COOMe), and 5.96 (1H, br s, H-3); ^{13}C NMR (CDCl$_3$) minor isomer: δ=18.56 (6-Me), 23.33 (2-Me), 32.05, 40.70 (C-5 and C-6), 52.08 (COOMe), 53.54 (C-1), 128.36 (C-3), 156.44 (C-2), 170.69 (COOMe), and 199.04 (C-4); major isomer: δ=19.83 (6-Me), 22.70 (2-Me), 32.88, 43.62 (C-5 and C-6), 52.25 (COOMe), 54.30 (C-1), 128.10 (C-3), 155.72 (C-2), 172.42 (COOMe), and 197.86 (C-4); MS *m/z* (rel intensity, %) 183 (M$^+$+1, 27), 182 (M$^+$, 31), 140 (62), 123 (50), 112 (base peak), 97 (25), 95 (19), and 53 (10). Found: C, 65.97; H, 7.74%. Calcd for C$_{10}$H$_{14}$O$_3$: C, 65.91; H, 7.74%.

4-Acetyl-3,5-dimethyl-2-cyclohexen-1-one (2d). Colorless liquid (an inseparable 1 : 4 mixture of stereoisomers (^{1}H and ^{13}C NMR), silica-gel column chromatography using hexane–ethyl acetate (3 : 1 v/v)); IR (neat) 2980, 1710, 1660, 1440, 1380, 1360, 1280, and 1160 cm^{-1}; ^{1}H NMR (CDCl$_3$) minor isomer: δ=1.07 (3H, d, $J_{\text{Me-}5}$=6.5 Hz, 5-Me), 1.90 (3H, br s, 3-Me), 2.29 (3H, s, MeCO), 3.46 (1H, d, $J_{4\text{-}5}$=4.4 Hz, H-4), 5.97 (1H, br s, H-2). Other signals overlap with those of the major isomer: major isomer: δ=1.08 (3H, d, $J_{\text{Me-}5}$=6.6 Hz, 5-Me), 1.88 (3H, br s, 3-Me), 2.0—2.6 (3H, m, H-5 and H-6), 2.25 (3H, s, MeCO), 3.13 (1H, d, $J_{4\text{-}5}$=5.9 Hz, H-4), and 5.99 (1H, br s, H-2); ^{13}C NMR (CDCl$_3$) minor isomer: δ=18.72 (5-Me), 23.74 (3-Me), 32.73 (MeCO), 33.49, 40.59 (C-5 and C-6), 58.86 (C-4), 128.40 (C-2), 157.07 (C-3), 199.06 (C-1), and 206.60 (MeCO); major isomer: δ=21.10 (5-Me), 23.17 (3-Me), 29.66 (MeCO), 32.18, 42.48 (C-5 and C-6), 61.90 (C-4), 128.52 (C-2), 155.72 (C-3), 197.83 (C-1), and 207.42 (MeCO); MS *m/z* (rel intensity, %) 167 (M$^+$+1, 25), 166 (M$^+$, 5), 124 (57), 123 (12), 109 (base peak), and 43 (47). Found: C, 72.06; H, 8.49%. Calcd for C$_{10}$H$_{14}$O$_2$: C, 72.26; H, 8.49%.

***trans*-3,5-Dimethyl-4-phenylsulfonyl-2-cyclohexen-1-one (2e).** Colorless solid (silica-gel column chromatography using hexane–ethyl acetate (3 : 1 v/v)); mp 93—95 °C (diethyl ether–hexane); IR (KBr) 1650, 1620, 1280, 1230, 1125, and 970 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.04 (3H, d, $J_{\text{Me-}5}$=7.0 Hz, 5-Me), 2.05 (1H, br d, J_{gem}=17.7 Hz, one of H-6), 2.08 (3H, br s, 3-Me), 2.78 (1H, m, H-5), 2.90 (1H, dd, J_{gem}=17.7 and $J_{6\text{-}5}$=5.4 Hz, the other of H-6), 3.66 (1H, br s, H-4), 6.14 (1H, br s, H-2), and 7.5—8.0 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=20.60 (5-Me), 25.34 (3-Me), 29.81, 38.95 (C-5 and C-6), 71.80 (C-4), 128.74, 129.59, 131.66, 134.47, 138.09 (Ph and C-2), 147.94 (C-3), and 196.26 (C-1); MS *m/z* (rel intensity, %) 264 (M$^+$, 3), 124 (10), 123 (base peak), 122 (20), and 95 (12). Found: C, 62.61; H, 6.05% (*m*/*z* 264.0820). Calcd for $C_{14}H_{16}O_3S$: C, 63.05; H, 6.11% (M, 264.0819).

10-Methylbicyclo[4.4.0]dec-5-ene-1,7-dione (3a).[10,23] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); IR (neat) 2980, 1710, 1660, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.47 (3H, s, 10-Me), 1.6—2.9 (10H, m, CH_2), and 5.86 (1H, d, $J_{6\text{-}8}$=1.9 Hz, H-6); ^{13}C NMR ($CDCl_3$) δ=22.91, 23.27, 29.91, 31.73, 33.61, 37.65 (Me, C-2,3,4,8, and C-9), 50.60 (C-10), 125.80 (C-6), 165.87 (C-5), 198.22 (C-7), and 210.99 (C-1); MS *m*/*z* (rel intensity, %) 178 (M^+, 69), 136 (63), 122 (base peak), 108 (68), 93 (76), 80 (54), 77 (61), and 55 (72); Found: C, 73.56; H, 7.85% (*m*/*z* 178.1006). Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92% (M, 178.0093).

9,10-Dimethylbicyclo[4.4.0]dec-5-ene-1,7-dione (3b).[23,24] Colorless liquid (an inseparable 7 : 8 mixture of cis and trans isomers (^1H NMR), silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); IR (neat) 2980, 1710, 1660, 1620, and 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (7/15×3H, d, $J_{\text{Me-5}}$=7.0 Hz, 9-Me), 1.05 (8/15×3H, d, $J_{\text{Me-5}}$=6.9 Hz, 9-Me), 1.34 (8/15×3H, s, 10-Me), 1.47 (7/15×3H, s, 10-Me), 1.6-2.8 (9H, m, CH_2 and CH), 5.87 (7/15H, br s, H-6), and 5.90 (8/15H, br s, H-6); ^{13}C NMR ($CDCl_3$) δ=15.85, 16.64, 16.77, 20.73 (9- and 10-Me), 22.91, 26.12, 31.10, 31.92, 33.00, 35.71, 37.11, 38.89, 41.32, 41.83 (C-2, 3, 4, 8, and C-9), 54.46, 54.79 (C-10), 124.70, 125.80 (C-6), 163.95, 167.22 (C-5), 197.86, 198.47 (C-7), 211.30, and 211.79 (C-1); MS *m*/*z* (rel intensity, %) 192 (M^+, 38), 150 (49), 136 (53), 135 (base peak), 107 (23), 94 (37), 93 (32), 91 (30), 79 (33), and 77 (25). Found: C, 74.51; H, 8.57% (*m*/*z* 192.1147). Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39% (M, 192.1149).

General Procedure for the Lewis Acid-Promoted Michael Reaction of Enones 1 with Silyl Enol Ethers. As a typical example, the Michael reaction of **1a** with 1-phenyl-1-(trimethylsilyloxy)ethene is described as follows: To a solution of **1a** (0.554 g, 2.68 mmol) in dichloromethane (1 ml) were added $TiCl_4$ (1 M in dichloromethane, 2.69 ml, 2.69 mmol) and Ti (*i*-PrO)$_4$ (0.305 g, 1.07 mmol) at −78 °C. After stirring at −78 °C for 30 min, the silyl enol ether (1.029 g, 5.36 mmol) was added. Stirring was continued at −50 °C for 16 h, the reaction mixture was poured into ice water, and then extracted with dichlormethane (30 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was purified by silica-gel column chromatography to give **4b** (0.783 g, 86%).

Reaction conditions for the formation of **4** and **7** and yields of **4b**, **c**, **e**, **f**, **i** are summarized in Table 2. The Michael adducts **4a**, **d**, **g**, **h**, and **7** were too labile to be purified through silica-gel column chromatography, therefore, they were subjected to the next cyclization procedure without further purification. No satisfactory analytical data were obtained because of the hygroscopic nature of **4b**, **c**, **e**, **f**, **i**. Therefore, analyses by HRMS are given. Spectral data of the purified Michael adducts are as follows.

Diethyl 2,6-Dioxo-6-phenylhexylphosphonate (4b). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (4 : 1 v/v)); IR (neat) 1710, 1680, 1250, 1025, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (6H, t, *J*=7.0 Hz, OEt), 2.40 (2H, quint, $J_{4\text{-}3}$=$J_{4\text{-}5}$=7.0 Hz, H-4), 2.77 (2H, t, $J_{3\text{-}4}$=7.0 Hz, H-3), 3.03 (2H, t, $J_{5\text{-}4}$=7.0 Hz, H-5), 3.09 (2H, d, $J_{\text{H-P}}$=22.7 Hz, H-1), 4.13 (4H, dq, $J_{\text{H-P}}$=8.0 and *J*=7.0 Hz, OEt), and 7.4—8.0 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=16.31 ($J_{\text{C-P}}$=5.9 Hz, OEt), 17.93 (C-4), 37.21 (C-5), 42.49 ($J_{\text{C-P}}$=127.2 Hz, C-1), 43.02 (C-3), 62.60 ($J_{\text{C-P}}$=6.8 Hz, OEt), 128.03, 128.61, 133.08, 136.84 (each Ph), 199.59 (C-6), and 201.67 ($J_{\text{C-P}}$=5.9 Hz, C-2); MS *m*/*z* (rel intensity, %) 3248 (M^+, 5), 327 (29), 308 (29), 207 (34), 179 (24), 170 (46), 151 (18), and 105 (base peak). HRMS Found: *m*/*z* 326.1282. Calcd for $C_{16}H_{23}O_5P$: M, 326.1282.

Diethyl 7,7-Dimethyl-2,6-dioxooctylphosphonate (4c). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (4 : 1 v/v)); IR (neat) 1710, 1250, 1025, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.12 (9H, s, *t*-Bu), 1.34 (6H, t, *J*=7.0 Hz, OEt), 1.84 (2H, quint, $J_{4\text{-}3}$=$J_{4\text{-}5}$=7.0 Hz, H-4), 2.53 (2H, t, $J_{3\text{-}4}$=7.0 Hz, H-3), 2.65 (2H, t, $J_{5\text{-}4}$=7.0 Hz, H-5), 3.07 (2H, d, $J_{\text{H-P}}$=23.1 Hz, H-1), and 4.16 (4H, dq, $J_{\text{H-P}}$=8.1 and *J*=7.0 Hz, OEt); ^{13}C NMR ($CDCl_3$) δ=16.35 ($J_{\text{C-P}}$=6.9 Hz, OEt), 17.68 (C-4), 26.41 (*t*-Bu), 35.12 (C-5), 42.36 ($J_{\text{C-P}}$=127.2 Hz, C-1), 43.05 (C-3), 44.03 (*t*-Bu), 62.58 ($J_{\text{C-P}}$=5.9 Hz, OEt), 201.69, ($J_{\text{C-P}}$=5.9 Hz, C-2), and 215.36 (C-6); MS *m*/*z* (rel intensity, %) 307 (M^++1, 39), 250 (11), 249 (base peak), 221 (18), 194 (12), 193 (14), and 151 (12). Found: C, 54.44; H, 9.16% (*m*/*z* 306.1598). Calcd for $C_{14}H_{27}O_5P$: C, 54.88; H, 8.90% (M, 306.1595).

Diethyl 4-Methyl-2,6-dioxo-6-phenylhexylphosphonate (4e). Colorless liquid (silica-gel column chromatography using ethyl acetate); IR (neat) 1710, 1680, 1250, 1025, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (3H, d, $J_{\text{Me-4}}$=6.2 Hz, 4-Me), 1.34 (6H, t, *J*=7.0 Hz, OEt), 2.6—2.9 (4H, m, H-3 and H-5), 3.0—3.1 (1H, m, H-4), 3.09 (2H, d, $J_{\text{H-P}}$=22.6 Hz, H-1), 4.13 (4H, dq, $J_{\text{H-P}}$=8.1 and *J*=7.0 Hz, OEt), and 7.4—8.0 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=16.33 ($J_{\text{C-P}}$=5.9 Hz, OEt), 20.09 (4-Me), 25.67 (C-4), 42.71 ($J_{\text{C-P}}$=126.2 Hz, C-1), 44.84 (C-5), 50.60 (C-3), 62.57 ($J_{\text{C-P}}$=6.9 Hz, OEt), 128.15, 128.61, 135.06 (each Ph), 199.42 (C-6), and 201.25 ($J_{\text{C-P}}$=6.9 Hz, C-2); MS *m*/*z* (rel intensity, %) 322 (M^+−18, 7), 221 (21), 220 (83), 192 (30), 164 (28), 152 (25), 125 (69), 123 (32), 108 (24), 105 (14), 97 (40), and 82 (24). HRMS Found: *m*/*z* 340.1440. Calcd for $C_{17}H_{25}O_5P$: M, 340.1438.

Diethyl 4,7,7-Trimethyl-2,6-dioxooctylphosphonate (4f). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (3 : 1 v/v)); IR (neat) 1710, 1260, 1025, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (3H, d, $J_{\text{Me-4}}$=6.2 Hz, 4-Me), 1.12 (9H, s, *t*-Bu), 1.34 (6H, t, *J*=7.0 Hz, OEt), 2.4—2.7 (5H, m, H-3, H-4 and H-5), 3.07 (2H, $J_{\text{H-P}}$=22.7 Hz, H-1), and 4.16 (4H, dq, $J_{\text{H-P}}$=8.0 and *J*=7.0 Hz, OEt); ^{13}C NMR ($CDCl_3$) δ=16.34 ($J_{\text{C-P}}$=5.9 Hz, OEt), 20.04 (4-Me), 24.87 (C-4), 26.31 (*t*-Bu), 42.56 ($J_{\text{C-P}}$=127.2 Hz, C-1), 42.72 (*t*-Bu), 44.13 (C-5), 50.47 (C-3), 62.54 ($J_{\text{C-P}}$=6.9 Hz, OEt), 201.69 ($J_{\text{C-P}}$=5.9 Hz, C-2), and 215.36 (C-6); MS *m*/*z* (rel intensity, %), and 321 (M^++1, 2), 320 (M^+, 1), 263 (50), 249 (base peak), 235 (11), 221 (40), 207 (15), 194 (27), 193 (31), 179 (29), 151 (29), 123 (26), and 57 (27). HRMS Found: *m*/*z* 320.1754. Calcd for $C_{15}H_{29}O_5P$: M, 320.1751.

Diethyl 7,7-Dimethyl-2,6-dioxo-4-phenyloctylphosphonate (4i). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (3 : 1 v/v)); IR (neat) 1710, 1250, 1025, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02 (9H, s, *t*-Bu), 1.24, 1.29 (each 3H, t, *J*=7.0 Hz, OEt), 2.8—3.0 (6H, m, H-1, H-3, and H-5), 3.74 (1H, quint, $J_{4\text{-}3}$=$J_{4\text{-}5}$=7.0 Hz, H-4), and 4.08 (each 2H, dq, $J_{\text{H-P}}$=8.0 and *J*=7.0 Hz, OEt); ^{13}C NMR ($CDCl_3$) δ=16.25 ($J_{\text{C-P}}$=6.8 Hz, OEt), 16.30 ($J_{\text{C-P}}$=5.9 Hz, OEt), 26.09 (*t*-Bu), 35.91 (C-4), 42.70 ($J_{\text{C-P}}$=126.2 Hz, C-1), 42.76 (*t*-Bu), 44.07 (C-5), 49.56 (C-3), 62.50 ($J_{\text{C-P}}$=6.9 Hz, OEt), 62.53

($J_{\mathrm{C-P}}$=5.9 Hz, OEt), 126.56, 127.56, 128.48, 143.71 (each Ph), 200.35 ($J_{\mathrm{C-P}}$=5.9 Hz, C-2), and 213.71 (C-6); MS *m*/*z* (rel intensity, %) 382 (M^+, 6), 364 (M^+-18, 26), 325 (34), 297 (26), 283 (36), 249 (base peak), 226 (77), 221 (34), 194 (29), 193 (31), 179 (61), 152 (21) ,151 (48), 131 (39), and 123 (41). HRMS Found: *m*/*z* 382.1910. Calcd for $\mathrm{C_{20}H_{31}O_5P}$: M, 382.1907.

General Procedure for the Intramolecular Horner-Emmons Olefinations of Michael Adducts 4 and 7 Leading to Cyclohexenones 5 and 8, Respectively. Two typical examples for the cyclization of purified **4b** and unpurified **4a** are described.

Cyclization of Purified 4b. To a suspension of sodium hydride (60% in mineral oil, 0.013 g, 0.32 mmol) in dry THF (3 ml) was added **4b** (0.11 g, 0.31 mmol) under nitrogen. After stirring at room temperature for 2 h, the mixture was acidified with 1 M hydrochloric acid and then extracted with dichloromethane (30 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The crude product was purified by silica-gel chromatography (hexane–ethyl acetate (2 : 1 v/v)) to give **5b** (0.055 g, 95%).

Cyclization of Unpurified 4a. To a suspension of sodium hydride (60% in mineral oil, 0.044 g, 1.1 mmol) in dry THF (6 ml) was added crude **4a**, which was obtained by the Michael reaction of **1a** (0.206 g, 1 mmol) with 2-(trimethylsilyloxy)propene (0.201 g, 1.5 mmol), at room temperature nitrogen. After stirring at room temperature for 2 h, the mixture was acidified with 1 M hydrochloric acid and then extracted with dichloromethane (30 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The crude product was purified by silica-gel chromatography (dichloromethane) to give **5a** (0.061 g, 54% in 2 steps).

Reaction conditions and yields of **5** and **8** are also summarized in Table 2. The known cyclohexenones were characterized mainly on the basis of ^{1}H NMR and ^{13}C NMR spectral data.

3-Methyl-2-cyclohexen-1-one (5a).[25—29] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.96 (3H, d, $J_{\mathrm{Me-2}}$=1.5 Hz, 3-Me), 1.9—2.1 (2H, m, H-5), 2.2—2.4 (4H, m, H-4 and H-6), and 5.88 (1H, q, $J_{\mathrm{2-Me}}$=1.5 Hz, H-2); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=22.58 (Me), 24.46 (C-5), 30.97 (C-4), 37.02 (C-6), 126.71 (C-2), 162.77 (C-3), and 199.76 (C-1).

3-Phenyl-2-cyclohexen-1-one (5b).[11,21] Colorless solids (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); mp 62—64 °C (diethyl ether–hexane) (lit,[21] 64.5—65.5 °C); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.15 (2H, quint, J_{5-4}=J_{5-6}=6.2 Hz, H-5), 2.48 (2H, t, J_{4-5}=6.2 Hz, H-4), 2.78 (2H, dt, J_{6-2}=1.5 and J_{6-5}=6.2 Hz, H-6), 6.42 (1H, t, J_{2-6}=1.5 Hz, H-2), and 7.3—7.6 (5H, m, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=22.82 (C-5), 28.12 (C-4), 37.28 (C-6), 126.09, 127.71, 128.76, 138.83 (each Ph), 129.97 (C-2), 159.79 (C-3), and 199.86 (C-1).

3-(*t*-Butyl)-2-cyclohexen-1-one (5c).[26,27] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); ^{1}H NMR ($\mathrm{CDCl_3}$)δ=1.13 (9H, s, *t*-Bu), 1.97 (2H, quint, J_{5-4}=J_{5-6}=6.2 Hz, H-5), 2.3—2.4 (4H, m, H-4 and H-6), and 5.96 (1H, t, J_{2-6}=1.1 Hz, H-2); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=28.28 (*t*-Bu), 29.72 (C-5), 31.94 (*t*-Bu), 36.89 (C-4), 37.51 (C-6), 123.06 (C-2), 173.85 (C-3), and 200.80 (C-1).

3,5-Dimethyl-2-cyclohexen-1-one (5d).[22,25,29] Colorless liquid (silica-gel column chromatography using dichloromethane); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.07 (3H, d, $J_{\mathrm{Me-5}}$=6.6 Hz, 4-Me), 1.96 (1H, br s, 3-Me), 2.0—2.5 (5H, m, H-4, 5, and H-6), and 5.87 (1H, br s, H-2); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=21.14 (5-Me), 24.38 (3-Me), 30.06 (C-5), 39.44 (C-4), 45.24 (C-6), 126.35 (C-2), 161.92 (C-3), and 200.02 (C1); MS *m*/*z* (rel intensity, %) 125 (M^++1, 5), 124 (M^+, 35), and 82 (base peak).

5-Methyl-3-phenyl-2-cyclohexen-1-one (5e).[15,17] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); (lit,[15] mp 34—36 °C); IR (neat) 2980, 1650, and 1600 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$)δ=1.17 (3H, d, $J_{\mathrm{Me-5}}$=6.6 Hz, 5-Me), 2.1—2.9 (5H, m, H-4, 5, and H-6), 6.41 (1H, br s, 2-H), and 7.3—7.6 (5H, m, Ph); MS *m*/*z* (rel intensity, %) 187 (M^++1, 10), 186 (M^+, 57), 144 (base peak), 116 (41), ane 115 (48). HRMS Found: *m*/*z* 186.1042. Calcd for $\mathrm{C_{13}H_{14}O}$: 186.1044.

3-(*t*-Butyl)-5-methyl-2-cyclohexen-1-one (5f). Colorless liquid (silica-gel column chromatography using dichloromethane); IR (neat) 2980, 1650, and 1605 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.08 (3H, d, $J_{\mathrm{Me-5}}$=6.2 Hz, 5-Me), 1.13 (9H, s, *t*-Bu), 1.90—2.22 (3H, m, H-4 and H-5), 2.39—2.53 (2H, m, H-6), and 5.94 (1H, d, J=1.8 Hz, H-2); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=21.18 (5-Me), 28.24 (*t*-Bu), 30.61 (C-5), 34.37 (C-4), 36.64 (*t*-Bu), 45.60 (C-6), 122.67 (C-2), 172.84 (C-3), and 201.00 (C-1); MS *m*/*z* (rel intensity, %) 166 (M^+, 79), 151 (34), 124 (base peak), 123 (48), 110 (31), 109 (96), 96 (83), 81 (52), and 57 (24). Found: C, 79.32; H, 10.75% (*m*/*z* 166.1360). Calcd for $\mathrm{C_{11}H_{18}O}$: C, 79.46; H, 10.92% (M, 166.1357).

3-Methyl-5-phenyl-2-cyclohexen-1-one (5g).[31] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.01 (3H, br s, 3-Me), 2.5—2.7 (4H, m, H-4, and H-6), 3.2—3.4 (1H, m, H-5), 5.98 (1H, br s, H-2), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=24.33 (Me), 39.02, 40.78, 43.86 (C-6), 126.58, 126.70, 128.78, 143.29 (each Ph), 126.97 (C-2), 161.59 (C-3), and 199.10 (C-1).

3,5-Diphenyl-2-cyclohexen-1-one (5h).[31,32] Colorless solids (silica-gel column chromatography using hexane–ethyl acetate (2 : 1 v/v)); mp 87—88 °C (diethyl ether–hexane) (lit,[32] 82 °C); IR (KBr) 1650, 1620, 1250, and 750 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=2.69 (1H, dd, J_{gem}=16.5 and J_{4-5}=12.1 Hz, one of H-4), 2.74 (1H, dd, J_{gem}=16.5 and J_{4-5}=5.5 Hz, the other of H-4), 2.90 (1H, ddd, J_{gem}=17.6, J_{6-5}=10.5, and J_{6-2}=2.2 Hz, one of H-6), 3.04 (1H, dd, J_{gem}=17.6 and J_{6-5}=4.4 Hz, the other of H-6), 3.43 (1H, m, H-5), 6.51 (1H, d, J_{2-6}=2.2 Hz, H-2), and 7.2—7.6 (10H, m, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=36.27 (C-5), 41.00 (C-4), 43.93 (C-6), 125.11, 126.16, 126.76, 127.08, 128.79, 128.82 (each Ph), 130.15 (C-2), 138.34, 143.19 (each Ph), 158.73 (C-3), and 199.17 (C-1); MS *m*/*z* (rel intensity, %) 249 (M^++1, 16), 248 (M^+, 49), 144 (base peak), 116 (35), 115 (37), 69 (47), 44 (34), and 28 (43). Found: C, 86.77; H, 6.49%. Calcd for $\mathrm{C_{18}H_{16}O}$: C, 87.06; H, 6.50%.

3-(*t*-Butyl)-5-phenyl-2-cyclohexen-1-one (5i).[31] Colorless prisms (hexane); mp 45-46 °C (lit,[31] 46 °C); IR (KBr) 1650, 1605, 1280, and 1240 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.14 (9H, s, *t*-Bu), 2.44 (1H, ddd, J_{gem}=18.0, J_{6-5}=11.4, and J_{6-2}=2.6 Hz, one of H-6), 2.57 (1H, dd, J_{gem}=16.5 and J_{4-5}=12.8 Hz, one of H-4), 2.68 (1H, br dd, J_{gem}=16.5 and J_{4-5}=4.8 Hz, the other of H-4), 2.70 (1H, br dd, J_{gem}=18.0 and J_{6-5}=4.4 Hz, the other of H-6), 6.05 (1H, d, J_{2-6}=2.6 Hz, H-2), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=28.26 (*t*-Bu), 34.24 (C-5), 36.85 (*t*-Bu), 41.53 (C-4), 44.23 (C-6), 122.89 (C-2), 124.95, 126.78, 128.78, 143.60 (each Ph), 172.64 (C-3), and 200.12 (C-1); MS *m*/*z* (rel intensity, %) 229 (M^++1, 10), 228 (M^+, 62), 213 (12), 171 (11), 124 (base peak), 109 (39), 96 (12), 81 (13), 57 (15). HRMS Found: *m*/*z* 228.1448. Calcd for $\mathrm{C_{16}H_{20}O}$: M, 228.1513.

Bicyclo[4.3.0]non-1-en-3-one (8a).[6,11] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (4:1 v/v)); ^{1}H NMR (CDCl$_3$) δ=1.1—2.8 (11H, m) and 5.91 (1H, br s, H-2); ^{13}C NMR (CDCl$_3$) δ=23.89, 29.27, 31.86, 32.83, 37.48, 43.14, 122.27 (C-2), 177.56 (C-1), and 199.96 (C-3).

5-Phenylbicyclo[4.3.0]non-1-en-3-one (8b). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (4:1 v/v)); IR (neat) 1665, 1620, and 1450 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.15—1.95 (4H, m, H-7 and H-8), 2.45—3.10 (6H, m, H-4, 5, 6, and H-9), 6.00 (1H, dd, $J_{2\text{-}4}$=4.0 and $J_{2\text{-}4}$=1.8 Hz, H-2), and 7.15—7.50 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=23.38 (C-8), 31.29, 32.02, 45.17, 48.18, 49.30, 122.37 (C-2), 127.01, 128.74, 142.64 (each Ph), 174.32 (C-1), and 199.29 (C-3); MS *m/z* (rel intensity, %) 213 (M$^+$+1, 8), 212 (M$^+$, 41), and 108 (base peak). Found: C, 84.30; H, 7.62% (*m/z* 212.1201). Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60% (M, 212.1200).

Bicyclo[4.4.0]dec-1-en-3-one (8c).[6,11] Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (4:1 v/v)); ^{1}H NMR (CDCl$_3$) δ=1.1—2.5 (13H, m), and 5.82 (1H, br s, H-2); ^{13}C NMR (CDCl$_3$) δ=25.59, 26.95, 29.20, 34.47, 35.58, 36.54, 37.93, 124.32 (C-2), 167.38 (C-1), and 200.12 (C-3); MS *m/z* (rel intensity, %) 151 (M$^+$+1, 5), 150 (M$^+$, 23), 122 (base peak), 108 (16), 94 (30), and 79 (22).

5-Methylbicyclo[4.4.0]dec-1-en-3-one (8d).[8,15,26] Colorless liquid (an inseparable 4:1 mixture of cis and trans isomers (^{1}H and ^{13}C NMR), silica-gel column chromatography using hexane–ethyl acetate (4:1 v/v)); IR (neat) 2980, 1660, 1620, and 1450 cm^{-1}; ^{1}H NMR (CDCl$_3$) cis isomer: δ=1.08 (3H, d, $J_{\text{Me-5}}$=6.5 Hz, 5-Me). Other signals overlap with those of the trans isomer; trans isomer: δ=1.00 (3H, d, $J_{\text{Me-5}}$=6.2 Hz, 5-Me), 1.2—2.6 (12H, m, H-4, 5, 6, 7, 8, 9, and 10), and 5.80 (1H, br s, H-2); ^{13}C NMR (CDCl$_3$) cis isomer: δ=19.48 (5-Me), 25.67, 26.84, 32.30, 35.16, 35.84, 45.05, 124.16 (C-2), 166.52 (C-1), and 200.09 (C-3); trans isomer: δ=17.26 (5-Me), 26.08, 28.08, 29.52, 31.39, 36.92, 42.20, 43.81, 122.59 (C-2), 169.17 (C-1), and 199.94 (C-3); MS *m/z* (rel intensity, %) 165 (M$^+$+1, 6), 164 (M$^+$, 29), 122 (base peak), 121 (25), 94 (33), 79 (23).

5-Phenylbicyclo[4.4.0]dec-1-en-3-one (8e). Colorless liquid (an inseparable 4:1 mixture of stereoisomers (^{13}C NMR), silica-gel column chromatography using hexane–ethyl acetate (4:1 v/v)); IR (neat) 1650, 1620, and 1450 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.0—3.0 (12H, m, H-4, 5, 6, 7, 8, 9, and H-10), 5.12 (1H, br s, H-2), and 7.1—7.4 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) major isomer: δ=25.41, 26.49, 32.31, 35.65, 43.97, 44.81, 47.64, 124.50 (C-2), 126.95, 127.51, 128.71, 142.56 (each Ph), 166.14 (C-1), and 199.09 (C-3); minor isomer: δ=26.10, 28.80, 30.22, 37.26, 37.65, 42.19, 45.53, 122.40 (C-2), 126.72, 127.45, 128.51, 142.56 (each Ph), 170.02 (C-1), and 199.76 (C-3); MS *m/z* (rel intensity, %) 227 (M$^+$+1, 10), 226 (M$^+$, 42), 123 (11), 122 (base peak). Found: C, 84.13; H, 8.02% (*m/z* 226.1358). Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02% (M, 226.1357).

General Procedure for Intramolecular Knoevenagel Condensations of Michael Adducts 4a, d, g Leading to Phosphinylcyclohexenones 6. As a typical example, the intramolecular Knoevenagel condensation of **4d** is described as follows: To a solution of crude adduct **4d**, which was obtained by the Michael reaction of **1b** (0.220 g, 1 mmol) with 2-(trimethylsilyloxy)propene (0.201 g, 1.5 mmol), in dichloromethane (3 ml) were added zinc bromide (0.27 g, 1.2 mmol) and triethylamine (0.167 ml, 1.2 mmol) at room temperature. After stirring at room temperature for 24 h, the reaction mixture was acidified with 1 M hydrochloric acid and then extracted with dichloromethane (30 ml×3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate (4:1 v/v)) to give **6b** (0.201 g, 77%).

Reaction conditions and yields of **6** are summarized in Table 2. No satisfactory analytical data were obtained because of their hygroscopic nature of **6**. Only analyses by HRMS are given.

Diethyl 2-Methyl-6-oxo-1-cyclohexenylphosphonate (6a). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (1:4 v/v)); IR (neat) 1670, 1575, 1225, 1025, and 950 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.33 (6H, t, J=7.0 Hz, OEt), 1.9—2.7 (9H, m, 2-Me, H-3, 4, and H-5), and 4.0—4.3 (4H, m, OEt); ^{13}C NMR (CDCl$_3$) δ=16.38 ($J_{\text{C-P}}$=6.8 Hz, OEt), 21.27 (C-4), 24.31 ($J_{\text{C-P}}$=4.9 Hz, 2-Me), 35.56 ($J_{\text{C-P}}$=5.7 Hz, C-3), 38.02 ($J_{\text{C-P}}$=6.9 Hz, C-5), 62.09 ($J_{\text{C-P}}$=5.9 Hz, OEt), 127.35 ($J_{\text{C-P}}$=181.9 Hz, C-1), 175.93 ($J_{\text{C-P}}$=8.8 Hz, C-2), and 196.51 ($J_{\text{C-P}}$=5.9 Hz, C-6); MS *m/z* (rel intensity, %) 247 (M$^+$+1, 19), 246 (M$^+$, base peak), 231 (24), 190 (53), 172 (24), and 120 (18). HRMS Found: *m/z* 246.1022. Calcd for $C_{11}H_{19}O_4P$: M, 246.1020.

Diethyl 2,4-Dimethyl-6-oxo-1-cyclohexenylphosphonate (6b). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (1:4 v/v)); IR (neat) 1650, 1570, 1220, 1015, 950 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.06 (3H, d, $J_{\text{Me-4}}$=5.9 Hz, 4-Me), 1.32 (6H, t, J=7.0 Hz, OEt), 1.9—2.6 (5H, m, H-3, 4, and H-5), 2.44 (3H, d, $J_{\text{H-P}}$=2.9 Hz, 2-Me), and 4.0—4.3 (4H, m, OEt); ^{13}C NMR (CDCl$_3$) δ=16.36 ($J_{\text{C-P}}$=6.9 Hz, OEt), 20.81 (4-Me), 24.18 ($J_{\text{C-P}}$=4.9 Hz, 2-Me), 28.54 (C-4), 43.82 ($J_{\text{C-P}}$=6.6 Hz, C-3), 46.11 ($J_{\text{C-P}}$=6.9 Hz, C-5), 61.88, 62.06 (each $J_{\text{C-P}}$=5.9 Hz, OEt), 126.80 ($J_{\text{C-P}}$=181.0 Hz, C-1), 175.19 ($J_{\text{C-P}}$=8.8 Hz, C-2), and 196.79 ($J_{\text{C-P}}$=6.9 Hz, C-6); MS *m/z* (rel intensity, %) 261 (M$^+$+1, 17), 260 (M$^+$, base peak), 245 (41), 217 (24), and 204 (23). HRMS Found: *m/z* 260.1176. Calcd for $C_{12}H_{21}O_4P$: M, 260.1176.

Diethyl 2-Methyl-4-phenyl-6-oxo-1-cyclohexenylphosphonate (6c). Colorless liquid (silica-gel column chromatography using hexane–ethyl acetate (1:2 v/v)); IR (neat) 1660, 1225, 1025, and 950 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.35 (6H, dt, $J_{\text{H-P}}$=7.0 Hz, OEt), 2.48 (3H, d, $J_{\text{H-P}}$=2.9 Hz, 2-Me), 2.6—3.4 (5H, m, H-3, 4, and H-5), 4.0—4.3 (4H, m, OEt), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=16.41 ($J_{\text{C-P}}$=6.9 Hz, OEt), 24.23 ($J_{\text{C-P}}$=5.9 Hz, 2-Me), 39.11 (C-4), 43.34 ($J_{\text{C-P}}$=5.7 Hz, C-3), 44.72 ($J_{\text{C-P}}$=7.8 Hz, C-5), 62.06, 62.28 (each $J_{\text{C-P}}$=5.8 Hz, OEt), 126.56, 128.70, 128.87, 134.75 (each Ph), 129.90 ($J_{\text{C-P}}$=162.4 Hz, C-1), 174.76 ($J_{\text{C-P}}$=8.8 Hz, C-2), and 196.13 ($J_{\text{C-P}}$=6.9 Hz, C-6); MS *m/z* (rel intensity, %) 323 (M$^+$+1, 24), 322 (M$^+$, base peak), 307 (18), 282 (17), 184 (21), 152 (19), 144, (36), 131 (19), and 125 (14). HRMS Found: *m/z* 322.1332. Calcd for $C_{17}H_{23}O_4P$: M, 322.1333.

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