Synthesis and Reactions of Ethyl 6-Aryl-3-ethoxy-6-oxo-2,4-hexadienoates

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Biologically interesting ethyl 6-aryl-3-ethoxy-6-oxo-2,4-hexadienoates (1) have been prepared by the Wittig reaction of [3-(ethoxycarbonyl)-2-ethoxy-2-propenylidene]triphenylphosphoranes (3a and 3b) and -arsorane (3c) with glyoxal monohydrates (5) and by oxidation of 6-aryl-3-ethoxy-6-hydroxy-2,4-hexadienoate (9) with activated manganese (IV) oxide supported by silica. Reaction of 1a with 3c gave 3-(4-chlorobenzoyl)-1,2-*trans* (and *cis*)-bis(1-ethoxy-2-ethoxycarbonylethenyl)cyclopropanes (6 and 7). When 1a was treated with a 1: 5 mixture of concentrated HCl and tetrahydrofuran at room temperature, 3-hydroxy-6-oxo-2,4-hexadienoate (10a) was obtained in 46% yield. Treatment of 1b with trifluoroacetic acid gave 5,6-dihydro-2*H*-pyran-2-one (12) in 53% yield together with 10b in 28% yield. When 1a was treated with 1 N ethanolic potassium hydroxide, 12 and 2*H*-pyran derivative (13) were obtained in 33% and 28% yields, respectively. Reaction of 1a with ammonium hydroxide and primary amines in the presence of a proton acid gave 2-oxo-1,2,5,6-tetrahydropyridines (14) in good yields. The mechanism of the formation of 6, 12, 13, and 14 is discussed.

Key words 6-aryl-3-ethoxy-6-oxo-2,4-hexadienoate; 2*H*-pyran-2-one; tetrahydropyridine; cyclopropane derivative

In the course of studies on [3+2]-annulation of allylidenetriphenylphosphoranes with α-halocarbonyl compounds, we found that the reaction of 2-ethoxy-(3-ethoxycarbonyl)allylidenetriphenylphosphorane (**3a**) with 2-bromo-4′-chloroacetophenone (**4**) afforded ethyl 6-(4-chlorophenyl)-3-ethoxy-6-oxo-2,4-hexadienoate (**1a**) in 3% yield, together with ethyl 4-(4-chlorophenyl)-2-ethoxy-1,3-cyclopentadiene-1-carboxylate (**2**) in 76% yield.[1a] Interestingly, **1a** was shown to have cytotoxic activity *in vitro* against L1210, immunosuppressive *in vitro* activity against lipopolysaccharide and concanavalin A stimulation, and inhibitory activity against carrageenin edema in the rat ($ED_{30}=46$ mg/kg).[2] The possible cytotoxic, immunosuppressive, and antiinflammatory actions of **1a** have led us to investigate an efficient synthetic methodology for this pharmacologically interesting compound. Herein we report the synthesis of **1** and the results of a study on the reaction of **1a** with the arsorane **3c** and with an appropriate acid or base.

Results and Discussion

Synthesis of 1 6-Aryl-6-oxo-3-ethoxy-2,4-hexadienoates **1** were prepared by two methods: one involves the Wittig reaction of phosphoranes (**3a** and **3b**) or arsorane (**3c**) with glyoxal monohydrates (**5**)[1b] (Chart 2) and the other involves oxidation of 6-aryl-3-ethoxy-6-hydroxy-2,4-hexadienoate (**9**), which was prepared from 6-oxo-3-ethoxy-2,4-hexadienoate (**8a**) and arylmagnesium bromide (Chart 3). Allylidenetriphenylphosphoranes (**3a** and **3b**) were prepared from allyltriphenylphosphonium bromides (**15a** and **15b**), which were synthesized according to the method described in the previous paper.[1a] Allylidenetriphenylarsorane **3c** was prepared from a corresponding arsonium bromide (**15c**), which was synthesized by a similar method to that used for the preparation of **3a**. Glyoxal monohydrates (**5a** and **5b**) were synthesized by oxidation of 4-chloro(or 4-iodo)acetophenone or 2-bromo-4′-chloro(or 4′-iodo)acetophenone with dimethyl sulfoxide (DMSO) in 47% hydrobromic acid.[3]

The Wittig reaction of the phosphoranes (**3a** and **3b**) with glyoxal monohydrates (**5a** and **5b**) at room temperature in tetrahydrofuran (THF) gave 2,4-hexadienoates (**1a—c**) in good yields, respectively (Chart 2). The structure **1** was confirmed on the basis of elemental analysis and mass, IR, and NMR spectral data. The IR spectrum of **1a** shows strong absorption bands at 1705 and 1625 cm^{-1} due to ester and ketone functions, respectively. The ^{1}H-NMR spectrum shows multiple signals at 7.92—7.89 and 7.48—7.44 ppm due to four aromatic protons. Three olefinic protons at 5.34 ppm as a singlet, and at 8.42 and 7.40 ppm as doublets ($J=15.4$ Hz) were assigned to the C-2, C-4 and C-5 olefinic protons, respectively. The coupling constant ($J=15.4$ Hz) between the C-4 and C-5 protons indicates that these protons are in the *trans*-configuration. However, the configuration of the double bond at the 2-position could not be determined on the basis of the ^{1}H-NMR spectral data. Finally, the double bonds at the 2- and 4-positions were confirmed to be in (2*E*,4*E*)-configuration by an X-ray crystal analysis of **1c**. The X-ray analytical data[4] and ORTEP structure[5] of **1c** are shown in Table 1, and Fig. 1.

On the other hand, the Wittig reaction of the arsorane (**3c**) with **5a** gave **1a** in 91% yield, together with an

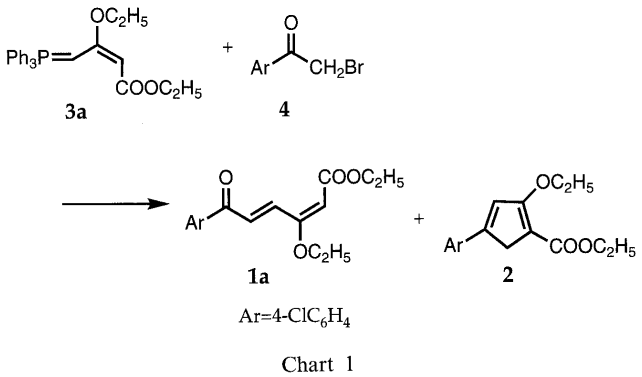

Chart 1

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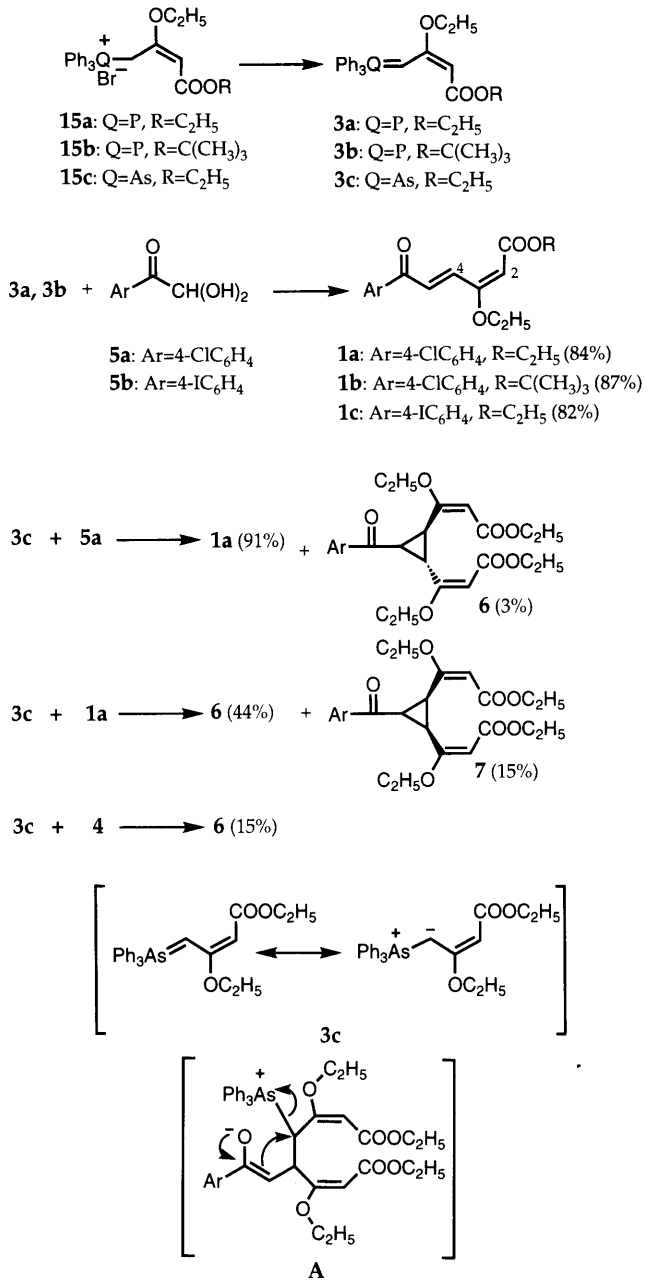


Chart 2

unexpected product (**6**) in 3% yield. Elemental analysis and mass spectral data showed **6** to have the molecular formula $C_{24}H_{29}ClO_7$. In the ^{1}H-NMR spectrum of **6**, two olefinic protons were observed at 5.14 and 4.99 ppm as singlets due to the vinylic protons of the 1-ethoxy-2-ethoxycarbonylethenyl function. Furthermore, three protons located at the cyclopropane ring appeared at 4.62 (J=6.3 and 6.0 Hz), 3.93 (J=9.8 and 6.0 Hz) and 3.25 (J=9.8 and 6.0 Hz) ppm as double-doublets. Four aromatic protons were observed at 7.97—7.94 and 7.41—7.38 ppm. From these data, the structure **6** was assigned to 3-(4-chlorobenzoyl)-1,2-*trans*-bis(1-ethoxy-2-ethoxycarbonylethenyl)cyclopropane. However, **6** was not detected in the reaction mixture obtained from the reaction of **3a** with **5a**.

Isolation of the unexpected product **6** produced by the reaction of **3c** with **5a** led us to study the reaction of **3c** with **1a** and **4** in order to investigate the mechanism of the formation of **6**. When **3c** was allowed to react with **1a** under the conditions described above, an additional new product **7**, with the molecular formula $C_{24}H_{29}ClO_7$ was obtained in 15% yield, together with **6** in 44% yield. The ^{1}H-NMR spectrum of **7** was similar to that of **6**, showing characteristic cyclopropane signals. The signal due to two vinylic protons of the 1-ethoxy-2-ethoxycarbonylethenyl function located at the 1- and 2-positions was observed at 5.07 ppm as a singlet. The signals observed at 1.32 and 1.25 ppm as triplets were assigned to methyl protons of the C-1 ethoxycarbonyl and the C-3 ethoxy functions, respectively. These data indicate that **7** is 3-(4-chlorobenzoyl)-1,2-*cis*-bis(1-ethoxy-2-ethoxycarbonylethenyl)cyclopropane with C_{2v}-symmetry. The reaction of the phosphorane (**3a**) with **1a** gave neither **6** nor **7**. When **3c** was allowed to react with **4** in the presence of potassium *tert*-butoxide in dichloromethane at −78 °C, **6** was obtained in 15% yield without formation of **7**.

On the basis of the reports that reaction of stabilized arsonium ylides with α,β-unsaturated ketones and esters gives cyclopropane derivatives,[6] the formation of **6** and **7** can be explained: the carbanion of ylide **3c** attacks the carbon at the 4-position of **1a**, giving an intermediate A, followed by elimination of triphenylarsine to give **6** and **7**. The reactivity of the arsorane was shown to differ from that of the phosphorane, indicating that the allylidenearsorane (**3c**) reacts regioselectively at the α-position rather than at the γ-position, compared with the allylidenephosphorane (**3a**).[1] The reaction described here will be useful for the synthesis of cyclopropane

Table 1. Crystal Data and Experimental Data for **1c**

Formula	$C_{16}H_{17}IO_4$
M.W.	400.21
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell dimension	
a/Å	18.464 (4)
b/Å	8.497 (2)
c/Å	10.466 (1)
β/°	96.85 (1)
V/Å^3	1630.0
Z	4
D_c/g·cm^{-3}	1.63
No. of reflections	
All	2946
Observed	2946
R	0.062
R_w	0.072

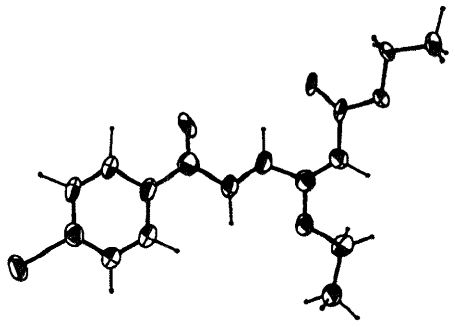


Fig. 1. An ORTEP Structure of **1c**

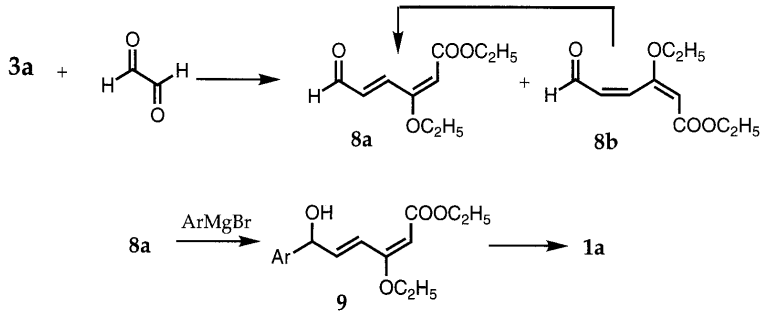
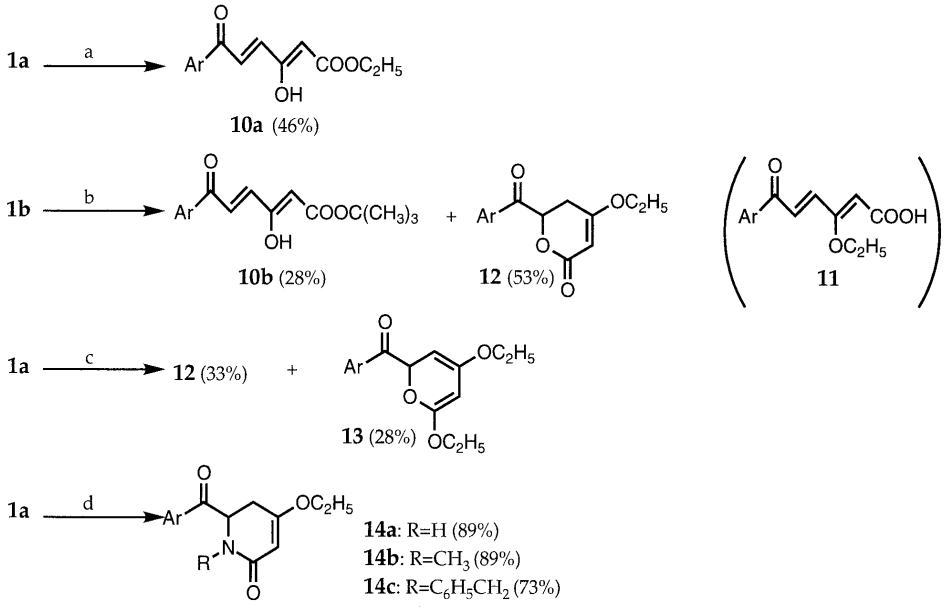


Chart 3



Reagents and conditions: a) conc. HCl : THF = 1 : 5 (v/v), r.t.; b) TFA, benzene, r.t.; c) 1*N* ethanolic KOH, 60 °C; d) NH_4OH or RNH_2, H^+, EtOH, r.t.

Chart 4

derivatives having three functional groups on the 1-, 2-, and 3-positions.

A second method for the preparation of **1a** is shown in Chart 3. Reaction of **3a** with 40% aqueous glyoxal at room temperature in THF gave a mixture of **8a** and **8b** in the ratio of 10 : 1, calculated from the isolation yields. In the ^{1}H-NMR spectrum of **8**, the C-4 and C-5 olefinic proton signals were observed at 6.70 and 8.39 ppm with the coupling constant of 16 Hz for **8a** and at 6.08 and 7.99 ppm with the coupling constant of 12 Hz for **8b**, indicating that the double bond at the 4-position has *E*-configuration in **8a** and *Z*-configuration in **8b**. Thus, the configuration of the double bonds at the 2- and 4-positions was assigned as (2*E*,4*E*) for **8a** and (2*E*,4*Z*) for **8b**, compared with the configuration of **1a**. Compound **8b** was converted to **8a** on treatment with hydrogen chloride in dry ether in a quantitative yield. When **8a** was treated with 4-chlorophenylmagnesium bromide, only the alcohol derivative **9** was obtained in 75% yield without the formation of the 1,4-adduct, indicating that the Grignard reaction was regioselective. Compound **9** was converted to **1a** in 76% yield on treatment with activated manganese(IV) oxide supported by silica.[7]

Reaction of 1a and 1b with Acid and Base; Conversion to Dihydro-2*H*-pyran-2-one, 2*H*-Pyran, and/or 2-Oxotetrahydropyridine Derivatives An attempt to obtain **10** and **11** by reaction of **1a** and **1b** with acid and caustic alkali afforded unexpected products, dihydro-2*H*-pyran-2-one (**12**) and/or 2*H*-pyran (**13**), together with the desired product **10**. Reaction of **1a** with amines gave only 2-oxo-tetrahydropyridines (**14**) (Chart 4). Compound **1a** was allowed to react with a (1 : 5, v/v) mixture of concentrated hydrochloric acid and THF at room temperature to give 3-hydroxy-2,4-hexadienoate (**10a**) in 46% yield. In the ^{1}H-NMR spectrum of **10a**, three olefinic protons were observed at 7.70 ppm (J = 15.8 Hz) as a doublet for the C-4 proton, 7.04 (J = 15.1 and 1.8 Hz) ppm as a double-doublet for the C-5 proton and 5.39 ppm as a singlet for the C-2 proton. The coupling constants indicate that the olefinic protons are in the *trans*-configuration in comparison with those of **1a**. The signal observed at 11.75 ppm (J = 1.8 Hz) was assigned to the enol proton at the 3-position and the low-field shift of this proton is consistent with the formation of a hydrogen

bond between the enolic hydroxy and ester carbonyl functions. Moreover, the nuclear Overhauser effect (NOE) observed between the C-2 and C-4 protons (17%) permitted us to establish the configuration of the double bond of the 2-position as 2*Z*. Additionally, the IR spectrum of **10a** shows an absorption band at 1595 cm^{-1} due to ester carbonyl, the low-wave number shift of which compared with the absorption band (1705 cm^{-1}) of the ester carbonyl group of **1a** also indicates the formation of the hydrogen bond. On the basis of these data, the configuration of the double bond at the 2- and 4-positions of **10a** was determined to be (2*Z*,4*E*). When **1b** was treated with trifluoroacetic acid (TFA) for 45 min at room temperature, 2*H*-pyran-2-one (**12**) was obtained in 53% yield, together with **10b** in 28% yield. However, the desired acid **11** was not obtained.

On the other hand, reaction of **1a** with 1 N ethanolic potassium hydroxide at 60 °C for 15 min gave the 2*H*-pyran derivative (**13**) in 28% yield together with **12** in 33% yield. Compound **13** was not converted to **12** on treatment with 1 N ethanolic potassium hydroxide, indicating that **12** and **13** were produced through independent pathways. Compound **12** has the molecular formula $C_{14}H_{13}ClO_4$, based on elemental analysis and mass spectral data. The IR spectrum of **12** shows absorption bands at 1695 and 1745 cm^{-1} due to lactone carbonyl and ketone functions, respectively. In the ^{1}H-NMR spectrum, the olefinic proton doublet at 5.10 ppm (J=0.9 Hz) was assigned to the C-3 proton. The C-5 methylene protons gave AB-type signals at 3.40 (J=17.0 and 3.7 Hz) and 3.29 ppm (J=17.0 and 8.0 Hz) as double-doublets. The methine proton at the 6-position appeared at 5.46 ppm (J=8.0, 3.7 and 0.9 Hz) as a double-double-doublet. Long-range coupling (J= 0.9 Hz) was observed between the C-3 and C-6 protons. From these data, **12** was assigned as 6-(4-chlorobenzoyl)-4-ethoxy-5,6-dihydro-2*H*-pyran-2-one. Compound **13** has the molecular formula $C_{16}H_{17}ClO_4$ from elemental analysis and mass spectral data. The IR spectrum of **13** shows absorption bands at 1710 and 1680 cm^{-1} due to a ketone function. In the ^{1}H-NMR spectrum, the two olefinic signals at 5.27 ppm as a singlet and 5.07 ppm (J=2.2 Hz) as a doublet were assigned to the C-3 and C-5 protons, respectively. The C-5 methylene proton signal appeared at 4.46 ppm (J=2.2 Hz). From these data, **13** was assigned as 2-(4-chlorobenzoyl)-4,6-diethoxy-2*H*-pyran. Treatment of **1a** with ammonium hydroxide and primary amines such as methylamine and benzylamine in the presence of a catalytic amount of proton acid gave the corresponding 2-oxo-1,2,5,6-tetrahydropyridines (**14a**—**c**) in good yields, respectively. The structure **14** was determined on the basis of elemental analysis and spectral data in comparison with those of **12**.

A possible mechanism for the formation of **12**, **13**, and **14** is proposed in Chart 5. Under alkaline conditions, **1a** is attacked by the hydroxide ion giving an intermediate B. Liberation of the ethoxy ion (path a) affords **12** *via* an intermediate C, while liberation of the hydroxide ion (path b) affords directly **13**. Thus, **12** and **13** seem to be produced by competitive reaction through pathways a and b. On the other hand, **1b** reacts with TFA giving acid D and then the acid D cyclizes to **12**. The formation of **14** can

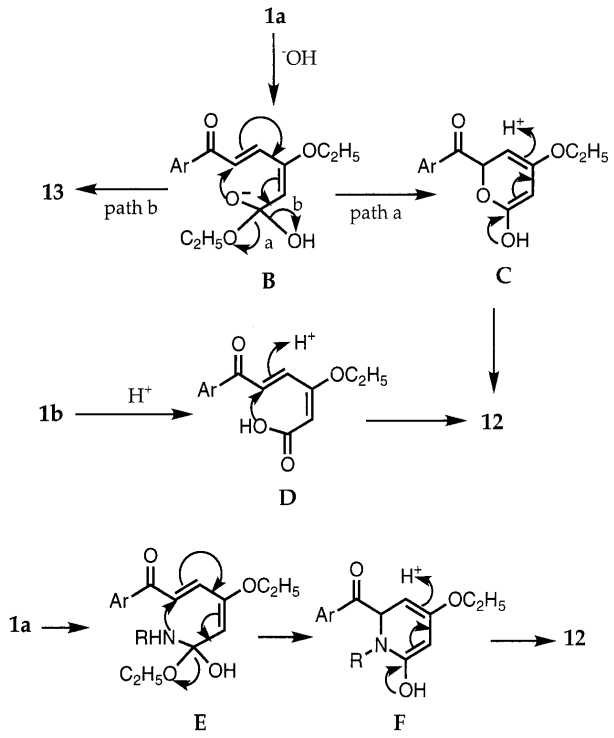


Chart 5

be explained by a route similar to that of **12**: **1a** reacts with amine in the presence of an acid to give an intermediate E which cyclizes to F, liberating selectively the ethoxy group. Isomerization of F affords the final product **12**.

In conclusion, a convenient synthesis of ethyl 6-(4-chlorophenyl)-3-ethoxy-6-oxo-2,4-hexadienoate (**1a**) and related compounds has been described. Compound **1a** was allowed to react with the arsorane **3c** to give 1-, 2-, and 3-tri-substituted cyclopropane derivatives (**6** and **7**) and was converted to 5,6-dihydro-2*H*-pyran-2-one and 2*H*-pyran derivatives (**12** and **13**) on treatment with ethanolic potassium hydroxide and to 2-oxo-1,2,5,6-tetrahydropyridines (**14**) on treatment with ammonium hydroxide and primary amines in the presence of a proton acid.

Experimental

General Methods Melting points were obtained on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260-30 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained on Hitachi R-90 (90 MHz), JEOL EX-270 (270 MHz), and Bruker AM 360 (360 MHz) spectrometers and the chemical shifts are expressed in δ (ppm) values with tetramethylsilane as an internal standard. Abbreviations of ^{1}H-NMR signal patterns are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; dt, double triplet; tt, triple triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra (HRMS) were obtained on a Hitachi M-80 spectrometer. TLC was carried out on silica gel (Kieselgel 60 F_{254}). Flash chromatography was performed on Wakogel C-300. The organic layers were dried over $MgSO_4$. CH_2Cl_2 was distilled from CaH_2. THF was distilled from sodium benzophenone ketyl.

Ethyl (2*E*,4*E*)-6-(4-Chlorophenyl)-3-ethoxy-6-oxo-2,4-hexadienoate (1a) This compound was prepared by three methods.

Method 1. Reaction of the Phosphorane **3a** with **5a**: A solution of **3a** (4.6 g, 11.0 mmol) in THF (100 ml) was added dropwise to a solution of **5a** (1.9 g, 10.0 mmol) in THF (50 ml) over 2.5 h at room temperature. The mixture was stirred for 6 h at room temperature and evaporated *in*

vacuo to give a solid, which was purified by silica gel chromatography with a 10:1 mixture of hexane and Et_2O to give **1a** (2.6 g, 84%). Recrystallization from hexane gave yellow needles, mp 118.5—119.6 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 8.42 (1H, d, J= 15.4 Hz), 7.92—7.89 (2H, m), 7.48—7.44 (2H, m), 7.40 (1H, d, J=15.4 Hz), 5.34 (1H, s), 4.19 (2H, q, J=7.1 Hz), 3.97 (2H, q, J=7.0 Hz), 1.45 (3H, t, J=6.8 Hz), 1.29 (3H, t, J=7.2 Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 190.2, 166.4, 163.2, 139.5, 136.0, 135.6, 130.2, 129.0, 127.7, 98.4, 64.2, 60.2, 14.3, 14.2. IR (KBr): 1705, 1625, 1595, 1580 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 306 (4.23), 226 (4.18). MS (EI) m/z: 308 (M^+). *Anal.* Calcd for $C_{16}H_{17}ClO_4$: C, 62.24; H, 5.55; Cl, 11.48. Found: C, 62.20; H, 5.41; Cl, 11.32.

Method 2. Reaction of the Triphenylarsorane **3c** with **5a**: A solution of **5a** (190 mg, 1.0 mmol) in THF (10 ml) was added to **3c**, which was prepared from **15c** (543 mg, 1.0 mmol) and *tert*-BuOK in THF (1.0 ml, 1.0 mmol), in CH_2Cl_2 at −78 °C. The resulting mixture was stirred for 30 min at −78 °C and then for an additional 9 h at room temperature and diluted with brine. The aqueous layer was extracted with CH_2Cl_2. The CH_2Cl_2 layers were combined, dried, and evaporated *in vacuo* to give a solid, which was purified by silica-gel chromatography with a 10:1 mixture of hexane and Et_2O to give **1a** (120 mg, 91%). Recrystallization from hexane gave yellow needles, mp 118.5—119.6 °C.

Method 3. Oxidation of **9**: Activated MnO_2 supported by SiO_2 (4.0 g, 3.33 mmol), prepared by the literature method,[7] was added to a solution of **9** (543 mg, 1.75 mmol) in $CHCl_3$ (30 ml). The mixture was stirred for 24 h at room temperature and filtered to remove insoluble materials. The filtrate was evaporated *in vacuo* to give crystals which were recrystallized from hexane to give pure **1a** (404 mg, 75%), mp 118.5—119.6 °C.

***tert*-Butyl (2*E*,4*E*)-6-(4-Chlorophenyl)-3-ethoxy-6-oxo-2,4-hexadienoate (1b)** This compound was prepared in 87% yield from **3b** (2.2 g, 5.0 mmol) and **5a** (933 mg, 5.0 mmol) according to method 1 used for the preparation of **1a**. Recrystallization from hexane gave pure **1b** as yellow crystals, mp 110.9—111.6 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 8.43 (1H, d, J=15.6 Hz), 7.93—7.91 (2H, m), 7.47—7.41 (3H, m), 5.28 (1H, s), 3.94 (2H, q, J=7.0 Hz), 1.49 (9H, s), 1.44 (3H, t, J=7.0 Hz). IR (KBr): 1710, 1625, 1595, 1580 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 307 (4.26), 225 (4.20). MS (FAB) m/z: 337 [$(M+H)^+$]. *Anal.* Calcd for $C_{18}H_{21}ClO_4$: C, 64.19; H, 6.28; Cl, 10.53. Found: C, 64.27; H, 6.22; Cl, 10.76.

Ethyl (2*E*,4*E*)-3-Ethoxy-6-(4-iodophenyl)-6-oxo-2,4-hexadienoate (1c) This compound was prepared in 82% yield from **3a** and **5b** according to method 1 used for the preparation of **1a**. Recrystallization from hexane gave pure **1c** as yellow columns, mp 104.2—105.4 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 8.42 (1H, d, J=15.8 Hz), 7.87—7.84 (2H, m), 7.68—7.66 (2H, m), 7.39 (1H, d, J=15.8 Hz), 5.34 (1H, s), 4.19 (2H, q, J=7.1 Hz), 3.96 (2H, q, J=7.0 Hz), 1.45 (3H, t, J=7.0Hz), 1.29 (3H, t, J=7.1 Hz). IR (KBr): 1710, 1620, 1585 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 311 (4.20), 228 (4.08). MS (FAB) m/z: 401 [$(M+H)^+$]. *Anal.* Calcd for $C_{16}H_{17}IO_4$: C, 48.02; H, 4.28; I, 31.71. Found: C, 47.83; H, 4.14; I, 31.68.

(*E*)-[2-Ethoxy-3-(ethoxycarbonyl)-2-propenylidene]triphenylphosphorane (3a) This compound was prepared from **15a** and aqueous NaOH according to the method described in the literature.[1] Yellow crystals, mp 166—167 °C [lit. mp 166—167 °C].

(*E*)-[2-Ethoxy-3-(*tert*-butoxycarbonyl)-2-propenylidene]triphenylphosphorane (3b) The crude **15b** syrup (59.4 g, 0.113 mol) was dissolved in H_2O (2000 ml) with stirring under ice-water cooling. The insoluble materials were filtered off and the filtrate was adjusted to pH 10 with 1 N NaOH. The precipitates were collected by filtration, washed with H_2O and dried at 60 °C *in vacuo*. Recrystallization from CH_2Cl_2–AcOEt gave **3b** as yellow crystals (30.6 g, 61%), mp 173—174 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 7.70—7.30 (15H, m), 4.61 (1H, br d, J=24.0 Hz), 4.33 (1H, d, J=6.8 Hz), 3.66 (2H, q, J=7.0 Hz), 1.50 (9H, s), 0.51 (3H, t, J=7.0 Hz). IR (KBr): 1650, 1500 cm^{-1}. MS (FAB) m/z: 447 [$(M+H)^+$]. *Anal.* Calcd for $C_{28}H_{31}O_3P$: C, 75.32; H, 7.00; P, 6.94. Found: C, 75.32; H, 7.23; P, 6.71.

(*E*)-[2-Ethoxy-3-(ethoxycarbonyl)-2-propenylidene]triphenylarsorane (3c) A solution of **15c** (543 mg, 1.0 mmol) in dry CH_2Cl_2 (10 ml) was cooled in a dry ice–MeOH bath. A solution of *tert*-BuOK in THF (1.0 ml, 1.0 mmol) was added to the cooled solution, and the mixture was stirred for 30 min at −78 °C and then allowed to stand at ambient temperature to give a precipitate. The precipitate was collected by filtration and recrystallized from CH_2Cl_2–AcOEt to give pure **3c** as yellow crystals (277 mg, 60%), mp 132.5—134.5 °C. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.75—7.33 (15H, m), 5.03 (1H, s), 4.33 (1H, s), 4.13 (2H, q, J=6.9 Hz), 3.73 (2H, q, J=6.9 Hz), 1.26 (3H, t, J=6.9 Hz), 0.58 (3H, t, J=6.9 Hz). IR (KBr): 1650, 1500 cm^{-1}. MS (FAB) m/z: 463 [$(M+H)^+$]. *Anal.* Calcd for $C_{26}H_{27}AsO_3$: C, 67.53; H, 5.89. Found: C, 67.18; H, 5.74.

2-Bromo-4′-chloroacetophenone (**4**) was prepared according to the method described in the literature.[3]

4-Chlorophenylglyoxal Monohydrate (5a) A 47% hydrobromic acid solution (3.0 ml) was added dropwise to a solution of **4** (2.33 g, 10 mmol) in DMSO (15 ml) over 20 min. The mixture was stirred for 90 min at 55 °C and poured onto ice (30 g). The aqueous layer was extracted with Et_2O. The ethereal solution was washed with brine, dried, and evaporated *in vacuo* to give **5a**. Recrystallization from AcOEt–hexane gave pure **5a** as colorless needles (1.68 g, 90%), mp 68.8—72.3 °C (lit.[3] mp 76—77 °C).

4-Iodophenylglyoxal Monohydrate (5b) A 47% hydrobromic acid solution (1.7 ml) was added dropwise to a solution of 4-iodoacetophenone (1.23 g, 5.0 mmol) in DMSO (8.5 ml) over 15 min. Work-up used for the preparation of **5a** gave **5b**. Recrystallization from AcOEt gave pure **5b** as colorless needles (1.32 g, 95%), mp 115.0—156.5 °C. MS (EI) m/z: 260 (M^+). *Anal.* Calcd for $C_8H_5IO_2 \cdot H_2O$: C, 34.56; H, 2.54; I, 45.64. Found: C, 34.50; H, 2.50; I, 45.59.

3-(4-Chlorobenzoyl)-1,2-*trans*-bis(1-ethoxy-2-ethoxycarbonylethenyl)-cyclopropane (6) Reaction of **3c** with **4**: A solution of **4** (233 mg, 1.0 mmol) in CH_2Cl_2 (2 ml) was added to **3c** over 2 h under dry ice–MeOH-cooling. The resulting mixture was stirred for 1 h at ambient temperature and then cooled to −78 °C. Additional *tert*-BuOK in THF (1.0 ml, 1.0 mmol) was slowly added to the cooled solution over 6 h. The mixture was allowed to stand at ambient temperature for 9 h with stirring, then poured into brine and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried and evaporated *in vacuo* to give a solid, which was purified by silica gel chromatography with a 10:1 mixture of hexane and Et_2O. The solid obtained was recrystallized from Et_2O to give pure **6** as colorless crystals (70 mg, 15%), mp 114.2—114.7 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 7.97—7.94 (2H, m), 7.41—7.38 (2H, m), 5.14 (1H, s), 4.99 (lH, s), 4.62 (1H, dd, J=6.3, 6.0 Hz), 4.18 (2H, q, J=7.1 Hz), 4.09 (2H, q, J=7.1 Hz), 3.93 (1H, dd, J=9.8, 6.0 Hz), 3.85 (2H, q, J=7.0 Hz), 3.72 (1H, m), 3.47 (1H, m), 3.25 (1H, dd, J=9.8, 6.3 Hz), 1.34 (3H, t, J=7.2 Hz), 1.28 (3H, t, J=7.2 Hz), 1.23 (3H, t, J=7.0 Hz), 1.15 (3H, t, J=7.0 Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 192.7, 168.5, 167.6, 167.3, 139.1, 135.8, 129.8, 128.6, 93.5, 93.3, 64.3, 64.1, 59.5, 59.4, 33.2, 29.6, 24.6, 14.4, 14.3, 14.1, 13.6. IR (KBr): 1715, 1700, 1595 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 252 (4.57). MS (EI) m/z: 464 (M^+). *Anal.* Calcd for $C_{24}H_{29}ClO_7$: C, 62.00; H, 6.29; Cl, 7.63. Found: C, 61.80; H, 6.20; Cl, 7.44.

Reaction of **3c** with **5a**: Reaction of **3c**, prepared from **15c** (1.8 g, 3.3 mmol), with **5a** (630 mg, 3.3 mmol) under the conditions described above gave **6** (80 mg, 3%), together with **1a** in 91% yield.

3-(4-Chlorobenzoyl)-1,2-*cis*-bis(1-ethoxy-2-ethoxycarbonyl)ethenylcyclopropane (7) Reaction of **1a** with **3c**: Reaction of **3c**, prepared from **15c** (543 mg, 1.0 mmol), with **1a** (309 mg, 1.0 mmol) under the conditions used for the preparation of **6** gave a solid, which was purified by silica gel chromatography with a 10:1 mixture of hexane and Et_2O to give **7** (72 mg, 15%), together with **6** (206 mg, 44%). Recrystallization from Et_2O–hexane gave pure **7** as colorless crystals, mp 74.9—75.7 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 8.00—7.97 (2H, m), 7.46—7.43 (2H, m), 5.07 (2H, s), 4.14—4.07 (4H, m), 3.82—3.67 (7H, m), 1.32 (6H, t, J=7.0 Hz), 1.25 (6H, t, J=7.0 Hz). IR (KBr): 1725, 1700, 1685, 1615 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 254 (4.30). HRMS (EI) m/z. Calcd for $C_{24}H_{29}ClO_7$: 464.1600 (M^+). Found 464.1601.

Ethyl (2*E*,4*E*)-3-Ethoxy-6-oxo-2,4-hexadienoate (8a) and Ethyl (2*E*,4*Z*)-3-Ethoxy-6-oxo-2,4-hexadienoate (8b) A solution of **3a** (5 g, 11.9 mmol) in THF (50 ml) was added dropwise to a mixture of 40% aqueous glyoxal (5 ml, 34.5 mmol) and THF (50 ml) with vigorous stirring. The resulting mixture was stirred for 30 min at room temperature. After removal of the THF, the residue was dissolved into Et_2O. The ethereal solution was washed with H_2O, dried, and evaporated *in vacuo* to give a mixture of **8a** and **8b**. The mixture was purified by silica gel chromatography with a 3:1 mixture of hexane and Et_2O. The first eluate gave pure **8a** as a viscous oil (1.0 g, 45%). This was allowed to stand at room temperature overnight to give crystalline **8a**. The second eluate gave **8b** (0.10 g, 4.5%).

8a: mp 37.0—39.0 °C. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 9.75 (1H, d, J=7.9 Hz), 8.39 (1H, d, J=16 Hz), 6.70 (1H, dd, J=16, 8.1 Hz), 5.33 (1H, s), 4.20 (2H, q, J=7.3 Hz), 3.94 (2H, q, J=7.0 Hz), 1.41 (3H, t, J=7.0 Hz), 1.30 (3H, t, J=7.3 Hz). IR (KBr): 2830, 1700, 1680, 1580, 1390 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 287 (3.77), 240 (3.77), 212 (3.75). MS (EI) m/z: 198 (M^+). *Anal.* Calcd for $C_{10}H_{14}O_4 \cdot 0.25\ H_2O$: C, 59.24; H, 7.21. Found: C, 59.29; H, 6.97. **8b**: mp 93.5—94.5 °C (from hexane).

^{1}H-NMR (270 MHz, $CDCl_3$) δ: 10.40 (1H, d, J=7.9 Hz), 7.99 (1H, d, J=12 Hz), 6.08 (1H, dd, J=12, 7.9 Hz), 5.34 (1H, s), 4.18 (2H, q, J=7.3 Hz), 4.00 (2H, q, J=7.3 Hz), 1.44 (3H, t, J=7.3 Hz), 1.30 (3H, t, J=7.3 Hz). IR (KBr): 2850, 1700, 1680, 1580, 1400 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 285 (3.81), 240 (3.75), 211 (3.77). MS (EI) m/z: 198 (M^+). *Anal.* Calcd for $C_{10}H_{14}O_4$: C, 60.59; H,7.12. Found: C, 60.80; H, 7.16.

When **8b** was treated with hydrochloric acid in Et_2O at room temperature for 1 h, it afforded **8a** in a quantitative yield.

Ethyl (2*E*,4*E*)-6-(4-Chlorophenyl)-3-ethoxy-6-hydroxy-2,4-hexadienoate (9) A solution of 4-chlorophenylmagnesium bromide, prepared from 4-chlorophenyl bromide (0.754 g, 4.0 mmol) and magnesium (0.100 g, 4.11 mmol), in THF (10 ml) was added dropwise to a solution of **8a** (0.792 g, 4.00 mmol) in THF (10 ml) at 0 °C over 15 min under an argon atmosphere. The mixture was stirred for 3 h at the same temperature, then poured into saturated aqueous NH_4Cl and the whole was extracted with Et_2O. The ethereal solution was washed with H_2O and brine, dried, and evaporated *in vacuo* to give a crystalline material, which was recrystallized from hexane to give pure **9** as colorless crystals (0.931 g, 75%), mp 75.5—76.5 °C. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.63 (1H, d, J=16 Hz), 7.32 (4H, m), 6.55 (1H, dd, J=16, 6.3 Hz), 5.34 (1H, d, J=6.3 Hz), 5.08 (1H, s), 4.14 (2H, q, J=7.2 Hz), 3.86 (2H, q, J=6.9 Hz), 2.42 (1H, br), 1.34 (3H, t, J=6.9 Hz), 1.27 (3H, t, J=7.0 Hz). IR (KBr): 3425, 2975, 1700, 1650, 1580, 1490, 1380, 1280 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 272 (4.32), 222 (4.13). *Anal.* Calcd for $C_{16}H_{19}ClO_4$: C, 61.84; H, 6.16; Cl, 11.41. Found: C, 61.49; H, 6.09; Cl, 11.15.

Ethyl (2*Z*,4*E*)-6-(4-Chlorophenyl)-3-hydroxy-6-oxo-2,4-hexadienoate (10a) A solution of **1a** (0.309 g, 1.0 mmol) in a 1 : 5 (v/v) mixture of concentrated HCl and THF (20 ml) was stirred for 8 h at room temperature. The mixture was diluted with brine (10 ml) and the whole was extracted with Et_2O. The ethereal solution was washed with brine, dried, and evaporated *in vacuo* to give a solid, which was recrystallized from hexane to give pure **10a** as yellow needles (0.130 g, 46%), mp 106.4—108.0 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 11.75 (1H, d, J=1.8 Hz), 7.98—7.95 (2H, m), 7.70 (1H, d, J=15.8 Hz), 7.50—7.47 (2H, m), 7.04 (1H, dd, J=15.1, 1.8 Hz), 5.39 (1H, s), 4.27 (2H, q, J=7.1 Hz), 1.33 (3H, t, J=7.0 Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 188.2, 172.1, 166.2, 140.1, 137.2, 135.7, 130.1, 129.2, 127.7, 97.7, 60.9, 14.2. IR (KBr): 1635, 1595 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 315 (4.26), 227 (4.00). MS (EI) m/z: 280 (M^+). *Anal.* Calcd for $C_{14}H_{14}ClO_4$: C, 59.90; H, 4.67; Cl, 12.63. Found: C, 60.05; H, 4.41; Cl, 12.48.

***tert*-Butyl (2*Z*,4*E*)-6-(4-Chlorophenyl)-3-hydroxy-6-oxo-2,4-hexadienoate (10b) and 6-(4-Chlorobenzoyl)-4-ethoxy-5,6-dihydro-2*H*-pyran-2-one (12)** Reaction of **1b** with TFA: A mixture of **1b** (337 mg, 1.0 mmol) and TFA (2 ml) in C_6H_6 (20 ml) was stirred for 45 min at room temperature and evaporated *in vacuo*. TFA contained in the residue was removed as the benzene azeotrope. The product obtained was purified by silica gel chromatography with a 10 : 1 mixture of hexane and Et_2O to give **10b** (85 mg, 28%) in the first eluate and **12** (150 mg, 53%) in the second eluate. Recrystallization of **10b** and **12** from hexane and ethyl acetate gave **10b** as yellow scales and **12** as colorless needles, respectively.

10b: mp 112.7—113.7 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 11.89 (1H, d, J=1.6 Hz), 7.99—7.96 (2H, m), 7.69 (1H, d, J=15.0 Hz), 7.50—7.47 (2H, m, Ar), 7.02 (1H, dd, J=15.0, 1.6 Hz), 5.31 (1H, s), 1.53 (9H, s). IR (KBr): 1635, 1600 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 316 (4.32), 229 (4.08). MS (FAB) m/z: 309 [$(M+H)^+$]. *Anal.* Calcd for $C_{16}H_{17}ClO_4$: C, 62.24; H, 5.55; Cl, 11.48. Found: C, 62.04; H, 5.27; Cl, 11.71. **12**: mp 144.7—145.5 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 7.90—7.86 (2H, m), 7.48—7.44 (2H, m), 5.46 (1H, ddd, J=8.0, 3.7, 0.9 Hz), 5.10 (1H, d, J=0.9 Hz), 4.17—4.09 (2H, m), 3.40 (1H, dd, J=17.0, 3.7 Hz), 3.29 (1H, dd, J=17.0, 8.0 Hz), 1.42 (3H, t, J=7.1 Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 193.7, 180.6, 171.9, 140.2, 134.7, 129.6, 129.1, 89.0, 74.6, 68.9, 40.6, 14.0. IR (KBr): 1745, 1695, 1625, 1595 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 253 (4.23). MS (EI) m/z: 280 (M^+). *Anal.* Calcd for $C_{14}H_{13}ClO_4$: C, 59.90; H, 4.67; Cl, 12.63. Found: C, 59.69; H, 4.55; Cl, 12.76.

2-(4-Chlorobenzoyl)-4,6-diethoxy-2*H*-pyran (13) Reaction of **1a** with KOH in EtOH: An 1 N KOH ethanol solution (2 ml) was added to a suspension of **1a** (309 mg, 1.0 mmol) in EtOH (1 ml). The mixture was stirred for 15 min in an oil bath at 60 °C and evaporated *in vacuo*. The residue was diluted with H_2O and the pH of the aqueous solution was adjusted to about 3 with 1 N HCl. The aqueous layer was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with H_2O, dried, and evaporated *in vacuo* to give a solid, which was purified by silica gel chromatography with a mixture of hexane and Et_2O to give **12** (102 mg, 33%) in the first eluate and **13** (78 mg, 28%) in the second eluate. Recrystallization of **13** from hexane gave colorless crystals, mp 80.8—81.9 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 8.06—8.03 (2H, m), 7.50—7.48 (2H, m), 5.27 (1H, s), 5.07 (1H, d, J=2.2 Hz), 4.46 (1H, d, J=2.2 Hz), 4.16—4.11 (2H, m), 3.77—3.70 (1H, m), 3.59—3.52 (1H, m), 1.48 (3H, t, J=7.1 Hz), 1.20 (3H, t, J=7.1 Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 194.9, 193.1, 186.5, 140.2, 134.8, 131.2, 128.9, 103.6, 78.4, 68.6, 67.0, 62.5, 15.3, 14.1. IR (KBr): 1710, 1680, 1605 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 251 (4.32). MS (EI) m/z: 308 (M^+). *Anal.* Calcd for $C_{16}H_{17}ClO_4$: C, 62.24; H, 5.55; Cl, 11.48. Found: C, 62.20; H, 5.45; Cl, 11.57.

6-(4-Chlorobenzoyl)-4-ethoxy-2-oxo-1,2,5,6-tetrahydropyridine (14a) Concentrated NH_4OH solution containing 1.8 M NH_4Cl (2 ml) was added to a solution of **1a** (309 mg, 1.0 mmol) in EtOH (30 ml). The mixture was stirred for 72 h at room temperature, and evaporated *in vacuo*. The residue was diluted with H_2O and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried, and evaporated *in vacuo*. This residue was purified by silica gel chromatography with AcOEt to give **14a** (249 mg, 89%). Recrystallization from AcOEt gave colorless needles, mp 133.8—134.5 °C. ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 7.91—7.88 (2H, m), 7.47—7.45 (2H, m), 6.06 (1H, s), 5.05 (1H, d, J=1.0 Hz), 4.55 (1H, d, J=10.5 Hz), 4.09—4.01 (2H, m), 3.59 (1H, dd, J=17.8, 2.5 Hz), 2.97 (1H, dd, J=17.8, 10.5 Hz), 1.42 (3H, t, J=7.2 Hz). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 196.4, 175.9, 173.5, 140.3, 134.4, 129.5, 129.1, 94.3, 67.4, 53.3, 41.7, 14.1. IR (KBr): 3200, 1700, 1685 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 252 (4.28). MS (EI) m/z: 279 (M^+). *Anal.* Calcd for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04; Cl, 12.67; N, 5.01. Found: C, 59.91; H, 4.77; Cl, 12.81; N, 5.23.

6-(4-Chlorobenzoyl)-4-ethoxy-1-methyl-2-oxo-1,2,5,6-tetrahydropyridine (14b) This compound was prepared in 89% yield from **1a** and methylamine according to the method used for the preparation of **14b**, mp 81.8—83.2 °C (from AcOEt). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.90 (2H, d, J=8.6 Hz), 7.47 (2H, d, J=8.6 Hz), 5.04 (1H, s), 4.63 (1H, dd, J=7.6, 4.0 Hz), 3.96 (2H, m), 3.36 (1H, dd, J=17, 4.0 Hz), 3.15 (1H, dd, J=17, 7.6 Hz), 2.84 (3H, s), 1.31 (3H, t, J=7.0 Hz). IR (KBr): 1685, 1640, 1590 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 253 (4.34). MS (EI) m/z: 293 (M^+). *Anal.* Calcd for $C_{15}H_{16}ClNO_3$: C, 61.33; H, 5.49; Cl, 12.07; N, 4.77. Found: C, 61.10; H, 5.38; Cl, 12.00; N, 4.69.

1-Benzyl-6-(4-chlorobenzoyl)-4-ethoxy-2-oxo-1,2,5,6-tetrahydropyridine (14c) This compound was prepared in 73% yield from **1a** and benzylamine according to the method used for the preparation of **14c**, mp 99.0—100.0 °C (from AcOEt). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.66 (2H, d, J=8.6 Hz), 7.36 (2H, d, J=8.6 Hz), 7.16—7.08 (5H, m), 5.11 (lH, s), 4.67 (1H, dd, J=7.3, 4.3 Hz), 4.62 (1H, d, J=16 Hz), 4.44 (1H, d, J=16 Hz), 3.96 (2H, m), 3.17 (1H, dd, J=17, 4.0 Hz), 3.06 (1H, dd, J=17, 7.0 Hz), 1.30 (3H, t, J=7.0 Hz). IR (KBr): 1685, 1635, 1590 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε): 253 (4.14). MS (EI) m/z: 369 (M^+). *Anal.* Calcd for $C_{21}H_{20}ClNO_3$: C, 68.20; H, 5.45; Cl, 9.59; N, 3.79. Found: C, 68.21; H, 5.30; Cl, 9.78; N, 4.02.

(*E*)-[2-Ethoxy-3-(ethoxycarbonyl)-2-propenyl]triphenylphosphonium Bromide (15a) This compound was prepared from ethyl 4-bromo-3-ethoxy-2-butenoate (60.0 g, 0.253 mol) and Ph_3P (66.4 g, 0.253 mol) according to the literature method.[1] Recrystallization from CH_3CN–AcOEt gave pure **10a** as colorless crystals (98.5 g, 78%), mp 137.5—139.5 °C (dec.). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 7.91—7.62 (15H, m), 5.64 (2H, br d, J=15.4 Hz), 5.05 (1H, d, J=2.4 Hz), 3.98 (2H, q, J=7.2 Hz), 3.67 (2H, q, J=7.2 Hz), 1.16 (3H, t, J=7.1 Hz), 1.04 (3H, t, J=7.0 Hz). IR (KBr): 1680, 1610 cm^{-1}. MS (FAB) m/z: 419 [$(M+H)^+-HBr$]. *Anal.* Calcd for $C_{26}H_{28}BrO_3P$: C, 62.53; H, 5.65; Br, 16.00; P, 6.20. Found: C, 62.57; H, 5.62; Br, 15.98; P, 6.06.

(*E*)-[3-(*tert*-Butoxycarbonyl)-2-ethoxy-2-propenyl]triphenylphosphonium Bromide (15b) This compound was prepared *in situ* from *tert*-butyl 4-bromo-3-ethoxy-2-butenoate (29.7 g, 0.112 mol) and Ph_3P (30.0 g, 0.114 mol) according to the method used for the preparation of **15a**. The crude **15b**, obtained as a syrup (59.4 g), was used for the preparation of **3b** without purification.

(*E*)-[2-Ethoxy-3-(ethoxycarbonyl)-2-propenyl]triphenylarsonium Bromide (15c) A mixture of ethyl 4-bromo-3-ethoxy-2-butenoate (5.9 g, 25.0 mol) and Ph_3As [8.1 g (95% purity); 25.0 mmol] was heated in an oil bath kept at 50 °C for 15 h under an argon atmosphere. The crystalline materials obtained were recrystallized from CH_2Cl_2–AcOEt to give pure **15c** as colorless crystals (12.5 g, 92%), mp 142.5—143.3 °C (dec.). ^{1}H-NMR (360 MHz, $CDCl_3$) δ: 7.80—7.65 (15H, m), 5.57 (2H, s), 5.03 (1H, s), 4.01 (2H, q, J=7.1 Hz), 3.63 (2H, q, J=7.0 Hz), 1.74 (3H, t, J=7.2 Hz), 1.10 (3H, t, J=7.0 Hz). IR (KBr): 1695, 1625 cm^{-1}. MS (FAB) m/z: 463 [$(M+H)^+-HBr$]. *Anal.* Calcd for $C_{26}H_{28}AsBrO_3$: C, 57.48; H, 5.19; Br, 14.71. Found: C, 57.27; H, 4.94; Br, 14.47.

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References and Notes

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