Allylidenetriphenylphosphorane as a Bifunctional Reagent: Synthesis of Cyclopentenones and α,β-Unsaturated Ketones with (3-(Alkoxycarbonyl)-2-ethoxy-2-propenylidene)triphenylphosphorane

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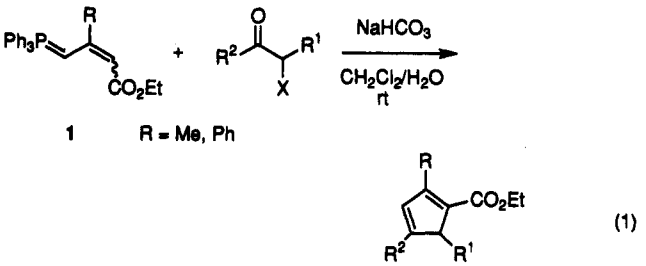
When (3-(ethoxycarbonyl)-2-ethoxy-2-propenylidene)triphenylphosphorane (**6**) was allowed to react with α-bromo ketones **8a-d** in dichloromethane in the presence of Cs_2CO_3 at room temperature, a [3 + 2] annulation occurred and led to the formation of the corresponding 2-ethoxycyclopentadienes **9a-d** in excellent yields. Similarly, bromo thioester **8g** underwent the annulation to give 4-(ethylthio)-cyclopentadiene **9g**. Secondary bromides 2-bromo-3-pentanone and 2-bromocyclohexanone also afforded tetrasubstituted cyclopentadienes **9e** and **9f** in moderate yields when 2 equiv of **6** was used. The annulation is believed to proceed through a sequence involving a stepwise alkylation at the γ position of **6** and an intramolecular Wittig reaction because of the fact that intermediate **11** was isolated. The resulting 2-ethoxycyclopentadienes **9a-g** were converted quantitatively into the corresponding cyclopentenones **10a-g** upon mild acid treatment. Furthermore, allylidenetriphenylphosphorane underwent a carbon elongation at both ends of the three-carbon unit via an alkylation–Wittig reaction sequence. (3-(*tert*-Butoxycarbonyl)-2-ethoxy-2-propenylidene)triphenylphosphorane (**7**) reacted first with alkyl halides and then with aldehydes in the presence of Cs_2CO_3 to give enol ethers **23a-f**, which were converted into α,β-unsaturated ketones **20**, **21**, and **25c-f** by hydrolysis of the enol ether and then decarboxylation. In this way, shogaol (**29**), the pungent principle component of ginger, was conveniently synthesized starting from 2-methoxy-4-methylphenol.

Allylidenetriphenylphosphoranes have two nucleophilic centers and react with various electrophiles at either the α or γ position depending on the electrophile and the substituents on the phosphorane. Aldehydes and ketones usually react at the α-position of allylidenephosphorane to give normal Wittig products,[2] although there are several reports describing substitution at both the α and γ positions.[3] Acylation occurs predominantly at the γ position,[4] and the regioselectivity of the alkylation of the phosphorane with alkyl halides remains uncertain because there are only a few precedents.[5]

We have investigated an annulation reaction that takes advantage of the bifunctional nature of the conjugated phosphoranes. Although it is well documented that allylidenephosphorane reacts with α,β-unsaturated aldehydes to give cyclohexadienes,[6] the synthetic utility of the phosphoranes in annulation reactions has been little explored. In a recent paper, we reported that the [3 + 2] annulation reaction of allylidenephosphoranes **1** with α-halo carbonyl compounds leads to the regioselective formation of cyclopentadienes with a variety of substitutents (eq 1).[7] The formation of five-membered carbocycles has been intensely studied in recent years.[8] In order to extend the scope and the utility of our [3 + 2] annulation reaction, we investigated use of an allylidenephoshorane having an alkoxy substituent at the 2-position. We expected that the reactions of the phosphorane with α-halo ketones would lead to the formation of alkoxycyclopentadienes, which could be readily converted into cyclopentenones upon mild acid treatment (Scheme 1). The occurrence of the annulation reveals that the initial alkylation takes place preferentially at the γ



(1)

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(6) (a) Büchi, G.; Wüest, H. *Helv. Chim. Acta.* **1971**, *54*, 1767. (b) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1973**, *106*, 3779. (c) Dauben, W. G.; Ipaktschi, J. *J. Am. Chem. Soc.* **1973**, *95*, 5088. (d) Dauben, W. G.; Hart, D. J.; Ipaktschi, J.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, 4425. (e) Padwa, A.; Brodsky, L. *J. Org. Chem.* **1974**, *39*, 1318. (f) Vedejs, E.; Bershas, J. P. *Tetrahedron Lett.* **1975**, 1359. (g) Martin, S. F.; Desai, S. R. *J. Org. Chem.* **1977**, *42*, 1664. (h) Hatanaka, M.; Yamamoto, Y.; Ishimaru, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1705.

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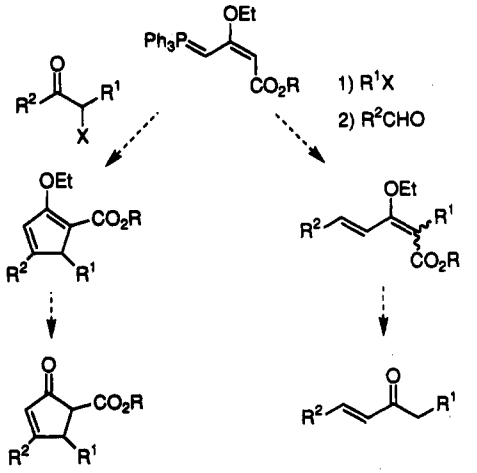
Scheme 1

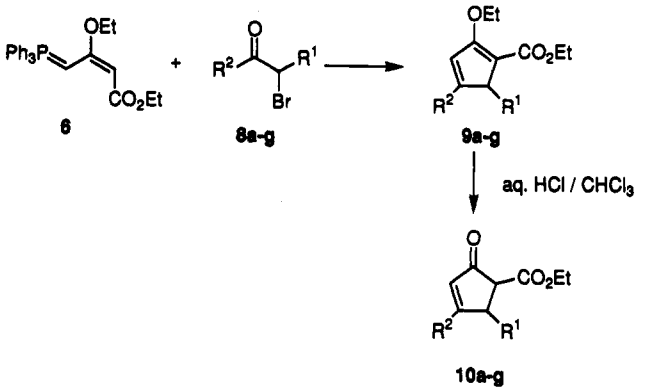


position of the phosphorane; subsequent intramolecular Wittig reaction leads to the formation of the cyclopentadiene. This result prompted us to investigate carbon elongation at both ends of the three-carbon unit of the phosphorane by an alkylation–Wittig reaction sequence, which would lead to the formation of α,β-unsaturated ketones. This paper describes the details of the syntheses of cyclopentenones and α,β-unsaturated ketones via (3-(alkoxycarbonyl)-2-ethoxy-2-propenylidene)triphenylphosphorane.[9]

Results and Discussion

Preparation of Starting Allylidenephosphoranes. (3-(Ethoxycarbonyl)-2-ethoxy-2-propenylidene)triphenylphosphorane (6) has previously been prepared by either addition of ethyl acetate to (diethoxyvinylidene)phosphorane[10] or acylation of (2-ethoxyallylidene)phosphorane with ethyl chloroformate.[4f] However, both procedures are inconvenient. We prepared allylidenephosphorane ethyl and *tert*-butyl esters 6 and 7 starting from ethyl enol ethers 2 and 3 of acetoacetic acid esters (eq 2). Bromination of 2 and 3 with NBS followed by treatment with triphenylphosphine gave phosphonium bromides 4 and 5, respectively. Phosphoranes 6 and 7 were conveniently obtained as fine yellow crystals by treatment of 4 and 5 with an aqueous NaOH solution. These phosphoranes exist as a single isomer in $CDCl_3$ solution. The C-1 protons of 6 and 7 appeared at 4.88 and 4.61 ppm, respectively, in the ^1H NMR spectra. The low-field shifts are consistent with the 2*E* configuration of 6 and 7. Howe observed similar shifts for the 2-methyl analogue prepared from 1 (R = Me).[11] In agreement with this assignment, 4 was regenerated when a $CDCl_3$ solution of 6 was treated with one drop of aqueous HBr.

Scheme 2

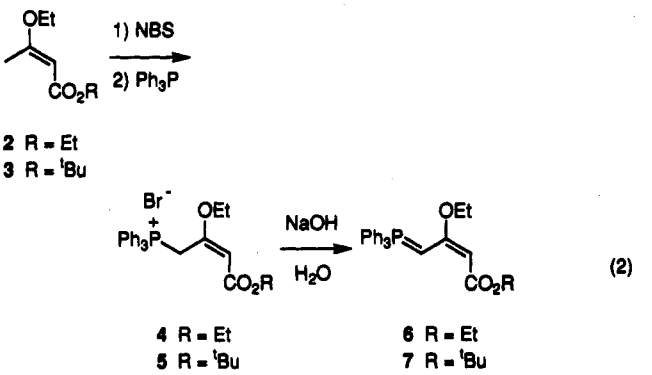


[a] For a–g, see Table 2.

Table 1. Conditions for Annulation Reaction of 6 or 4 with Phenacyl Bromide[a]

entry	reagent (equiv)	base (equiv)	solvent	yield of 9a %
1	6 (1.0)	Cs_2CO_3 (0.6)	CH_2Cl_2	92
2	6 (1.0)	Cs_2CO_3 (1.0)	CH_2Cl_2	70
3	6 (1.0)	DIPEA (1.2)	CH_2Cl_2	85
4	6 (1.0)	DIPEA (1.2)	THF	71
5	6 (1.0)	DIPEA (1.2)	DMF	51
6	6 (1.0)	*t*-BuOK (1.0)	THF	83
7	6 (2.0)		CH_2Cl_2	90[b]
8	4 (1.0)	DIPEA (2.3)	CH_2Cl_2	62

[a] All reactions were carried out at 30 °C for 48 h under N_2. [b] Isolated yield based on the amount of phenacyl bromide.



(2)

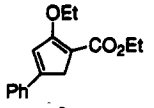
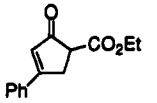
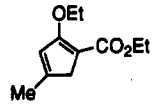
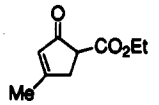
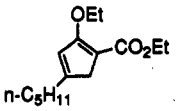
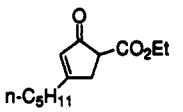
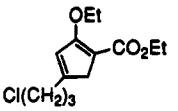
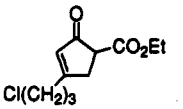
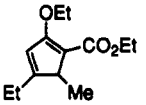
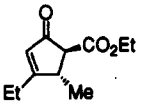
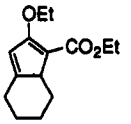
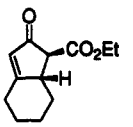
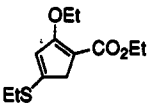
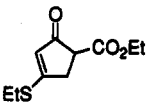
Synthesis of Cyclopentenone. Phosphonium bromide 4 was first subjected to the annulation reaction with phenacyl bromide in a heterogeneous medium of saturated aqueous $NaHCO_3$ and dichloromethane in a manner similar to that reported previously.[7] However, no formation of ethoxycyclopentadiene was observed. Isolation of 2 from the reaction mixture indicated facile hydrolysis of phosphonium bromide 4 in the aqueous medium. The desired annulation did occur under anhydrous conditions (Scheme 2). Several of the reaction conditions used are listed in Table 1. When phosphorane 6 was allowed to react with phenacyl bromide at 30 °C in the presence of a base, such as diisopropylethylamine (DIPEA) or Cs_2CO_3, the expected ethoxycyclopentadiene 9a was produced. The best results were obtained with 0.6 equiv of Cs_2CO_3[12] as the base in dichloromethane (entry 1). Without base,

(8) (a) For excellent reviews, see: Ramaiah, M. *Synthesis* **1984**, 529. Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1. Shore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991, Vol. 5, p 1037. (b) Curran, D. P. *Synthesis* **1988**, 417, 489. (c) Tius, M. A.; Astrab, D. P.; Fauq, A. H.; Ousset, J.-B.; Trehan, S. *J. Am. Chem. Soc.* **1986**, *108*, 3438. (d) Chamberlin, A. R.; Bloom, S. H.; Cervini, L. A.; Fotsch, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 4788. (e) Beak, P.; Burg, D. A. *J. Org. Chem.* **1989**, *54*, 1647. (f) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286. (g) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113. (h) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (i) Hirst, G. C.; Howard, P. N.; Overman, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 1514. (j) Mathau, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1264. (k) Ejiri, S.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, [illegible]. For preliminary reports of this work, see: Hatanaka, M.; Himeda, Y.; Ueda, I. *Tetrahedron Lett.* **1991**, *32*, 4521. Hatanaka, M.; Imashiro, R.; Ueda, I. *Chem. Lett.* **1992**, 2253.

(10) Bestmann, H.-J.; Saalfrank, R. W. *Chem. Ber.* **1976**, *109*, 403.

(11) Howe has reported that (3-(ethoxycarbonyl)-2-methyl-2-propenylidene)triphenylphosphorane exists as a equilibrium mixture of the *Z* and *E* conformers in a $CDCl_3$ solution. The C-1 proton for the major *Z*-conformer absorbed at lower field (5.58 ppm) than that (2.89 ppm) for the minor *E* conformer. Howe, R. K. *J. Am. Chem. Soc.* **1971**, *93*, 3457.

Table 2. Syntheses of 2-Ethoxycyclopentadienes 9 and Cyclopentenones 10

		2-ethoxycyclopentadiene				cyclopentenone	
entry	bromide	method[a]	time, h	yield, %	product	yield, %	product
1	$PhCOCH_2Br$ (8a)	A	48	92	 **9a**	99	 **10a**
2	$MeCOCH_2Br$ (8b)	A	48	84	 **9b**	91	 **10b**
3	$n\text{-}C_5H_{11}COCH_2Br$ (8c)	A	48	81	 **9c**	98	 **10c**
4	$Cl(CH_2)_3COCH_2Br$ (8d)	A	48	86	 **9d**	92	 **10d**
5	EtCOCHMe Br (8e)	A	72	36	 **9e**	98	 **10e**[c]
6		B	72	51[b]			
7	 (8f)	A	48	20	 **9f**	92	 **10f**[c]
8		B	72	47[b]			
9	$EtSCOCH_2Br$ (8g)	A	72	72	 **9g**	98	 **10g**

[a] All reactions were carried out in dichloromethane at 30 °C under N_2. Method A: in the presence of 0.6 equiv of Cs_2CO_3. Method B: 2 equiv of phosphorane 6. [b] Isolated yield based on the amount of halide. [c] Compounds 10e and 10f were obtained mainly in a trans form with over 95% selectivity.

2 equiv of phosphorane 6 gave a 90% yield of 9a (entry 7). Furthermore, the annulation also occurred when phosphonium bromide 4 was treated with phenacyl bromide and 2.3 equiv of DIPEA in dichloromethane; a 62% yield of 9a was obtained (entry 8). Cyclopentadiene 9a was converted quantitatively into cyclopentenone 10a upon treatment with diluted aqueous HCl.

The annulation reaction is applicable to the preparation of a variety of 2-ethoxycyclopentadienes, as illustrated in Table 2. Primary halides reacted with 6 in dichloromethane in the presence of 0.6 equiv of Cs_2CO_3 to give good to excellent yields of the corresponding cyclopentadienes (Table 2, entries 1–4). Secondary halides also underwent the annulation, although reaction times longer than those required for primary halides were necessary. In these cases, improved yields were obtained when 2 equiv of phosphorane 6 were used in the absence of Cs_2CO_3. In this way, a fused ring system could be constructed with 2-bromocyclohexanone (entry 8). Furthermore, α-bromo thioester also reacted with 6 to afford 4-(ethylthio)-cyclopentadiene 9g.

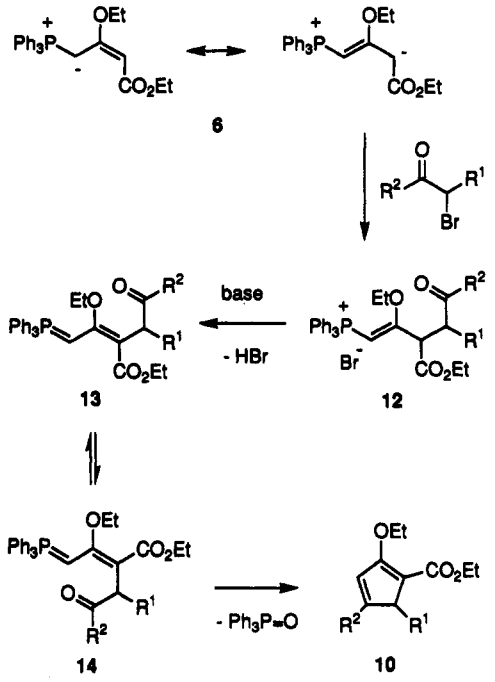
The resulting ethoxycyclopentadienes showed UV absorption maxima at 302–305 nm for the 4-alkylcyclopentadienes and at 342 nm for 9a due to the conjugated dienoic ester. In the ^1H NMR spectra of the cyclopentadienes, the C-3 olefinic protons were observed at 6.12–6.29 ppm for the 4-alkylcyclopentadienes and at 6.90 ppm for 9a. Furthermore, the 5-methyl protons of 9e appeared at 1.24 ppm as a doublet (J = 7.6 Hz). These data indicate that the ethoxycyclopentadienes have the double bonds fixed at the 1- and 3-positions, in analogy with the corresponding 2-methylcyclopentadienes previously reported.[7] Although the propensity of cyclopentadienes to undergo 1,5-sigmatropic migration has been reported,[13] the 2-ethoxycyclopentadienes prepared above are stable for at least several weeks at room temperature and resist the migration. For example, compound 9b was recovered unchanged after being heated in refluxing toluene for 24 h.

The resulting ethoxycyclopentadienes underwent conversion into the corresponding cyclopentenones when treated with aqueous HCl (Table 2). Cyclopentenones 10 can be also produced in a one-pot procedure from phosphorane 6 without isolation of the cyclopentadienes

(12) The use of 1 equiv of Cs_2CO_3 reduced the yield to 70% (entry 2). In this case, the reaction mixture became dark green, probably because of the formation of a cyclopentadienyl anion.

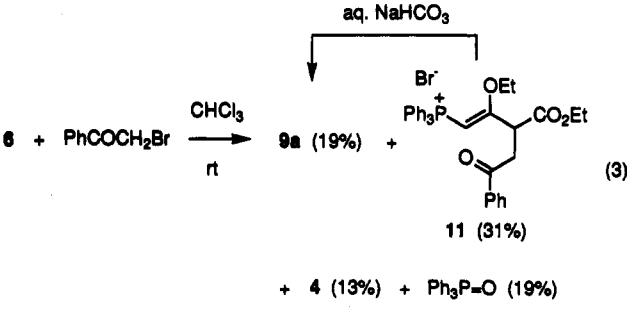
(13) McLean, S.; Hynes, P. *Tetrahedron* **1965**, *21*, 2313, 2343.

Scheme 3



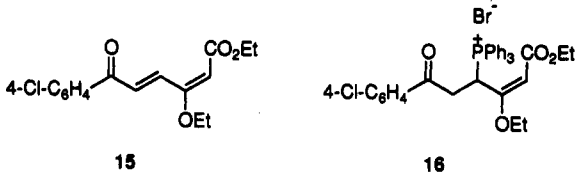
by treatment of the reaction mixture with aqueous HCl. In this way, **9a** was obtained in 81% yield from **6**.

In order to elucidate a plausible mechanism, phosphorane **6** was allowed to react with1 equiv of phenacyl bromide in chloroform at room temperature for 12 h. Preparative HPLC of the reaction mixture on a GPC column gave **9a** (19%), **11** (31%), **4** (13%), and triphenylphosphine oxide (19%) together with recovered phenacyl bromide (22%) (eq 3). The structure of alkylated phosphonium bromide



(3)

11 was determined by ^{1}H NMR. Compound **11** was quantitatively converted into **9a** upon being shaken in dichloromethane with saturated aqueous $NaHCO_3$ solution. These results indicate that the annulation is stepwise as shown in Scheme 3. The first step must be alkylation of the carbanion of the 1,4-dipolar resonance form of **6** to give **12**, which transformed into the phosphorane by transylidation with **6** or an external base. The resulting phosphorane may be an equilibrium mixture of **13** and **14**.[14] Intramolecular Wittig reaction furnishes cyclopentadiene **9**. The high yield of cyclopentadienes implies that the alkylation takes place predominantly at the γ-position of the phosphorane. In an effort to detect the α-alkylation product, compound **15** was isolated in 3% yield along with 76% yield of cyclopentadiene **10** (R^1 = H, R^2 = 4-ClC_6H_4) when *p*-chlorophenacyl bromide was allowed to react with 2 equiv of **6** in dichloromethane. Compound **15** may arise from initial alkylation at the α-position to form **16** and subsequent elimination of triphenylphosphine and HBr. Similar olefin formation from acylphosphorane and α-halo ketones has been reported to occur smoothly.[15] Thus, the very low yield of **15** in comparison with that of the cyclopentadiene is further evidence for the highly regioselective alkylation at the γ-position of the phosphorane.



Synthesis of α,β-Unsaturated Ketone. Taking advantage of the highly regioselective γ-alkylation of **6**, we next investigated the synthesis of α,β-unsaturated ketones by the carbon elongation of both ends of the three-carbon unit of the phosphorane via an alkylation–Wittig reaction sequence. Alkylation of phosphorane **6** with benzyl bromide was best carried out in DMF at room temperature to give phosphonium bromide **17a**, which was, without isolation, treated with *t*-BuOK and then benzaldehyde for 40 h at room temperature to afford **18a** as a mixture of two isomers (66 and 18% yields) (Scheme 4). The olefinic protons of both isomers have large coupling constants (J = 16 Hz) in the ^{1}H NMR spectra. The C-4 proton of the major isomer was observed at lower field than that of the minor isomer, probably because of the shielding effect of the neighboring ester group.[16] Thus, the structures of the isomers were assigned as (2*E*,4*E*)-**18a** and (2*Z*,4*E*)-**18a** for the major and minor isomer, respectively. Hydrolysis of enol ethers (2*E*,4*E*)-**18a** and (2*Z*,4*E*)-**18a** was accomplished by treatment with sulfuric acid on wet SiO_2 in dichloromethane[17] to give trans keto ester **19a** as a keto–enol tautomeric mixture in 95 and 89% yields, respectively. A similar alkylation–Wittig reaction of **6** with benzyl bromide and hexanal gave **18b** as a mixture of the geometrically isomeric enol ethers. The mixture was converted quantitatively into keto ester **19b**, which exists mainly in a keto form.

Heating **19a** at 140 °C with sodium chloride in wet DMSO[18] accomplished the decarboxylation and gave the desired α,β-unsaturated ketone **20** in 52% yield. However, attempted decarboxylation of **19b** in a similar manner resulted in the attendant formation of β,γ-unsaturated ketone **22** (13%) along with **21** (40%).

Finally, a convenient route to α,β-unsaturated ketones from phosphorane *tert*-butyl ester **7** was established (Scheme 5). In a one-pot procedure, phosphorane **7** was allowed to react with bromides in DMF at room temperature for 24 h, and then the mixture was treated with Cs_2CO_3 and hexanal at 60 °C for 24 h. The resulting enol ethers **23** were hydrolyzed with wet SiO_2 to give trans keto esters **24**. Treatment of **24** with trifluoroacetic acid and decarboxylation of the resulting acid gave the correspond-

(14) The phosphorane can be considered to exist as a mixture of two conformers, **13** and **14**, from the fact that **7** produces two isomers (2*E*,4*E*)-**18** and (2*Z*,4*E*)-**18** via an alkylation–Wittig reaction sequence. Although we could not separate **13** and **14**, these conformers must be in equilibrium (see ref 11).

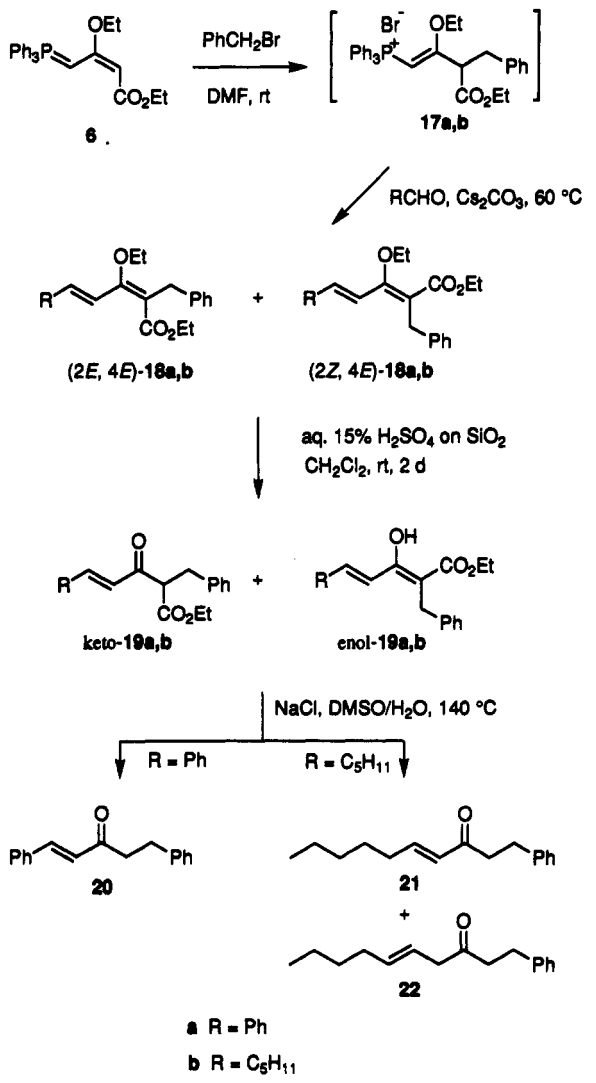
(15) Bestmann, H.-J.; Haberlein, H.; Pils, I. *Tetrahedron* **1964**, *20*, 2079. Bestmann, H.-J.; Seng, F.; Shulz, H. *Chem. Ber.* **1963**, *96*, 465.

(16) A similar low-field shift has been observed for the C-1 proton of ethyl (2*E*,4*E*)-2-benzyl-3-methyl-5-phenyl-2,4-hexadienoate: Wiley, R. H.; Crawford, T. H.; Staples, C. S. *J. Chem. Soc.* **1962**, 1535.

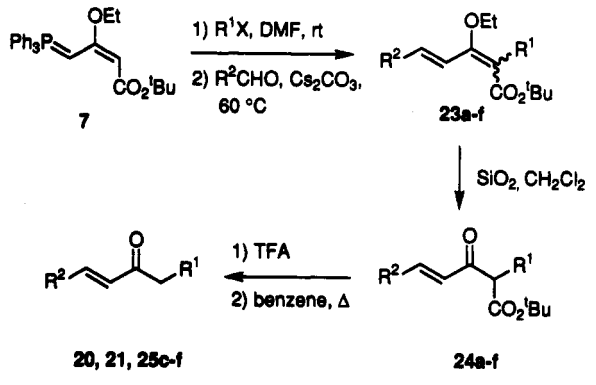
(17) Huet, F.; Lechevallier, A.; Pallet, M.; Conia, J. M. *Synthesis* **1978**, 63.

(18) Krapcho, A. P. *Synthesis* **1982**, 805, 893.

Scheme 4



Scheme 5



[a] For a–f, see Table 3.

ing trans α,β-unsaturated ketones. Representative examples are listed in Table 3. In this way, **24b** gave **21** exclusively without attendant formation of **22**. Thus, allylidenetriphenylphosphorane **7** was alkylated predominantly at the γ-position with various alkyl halides to provide a convenient route to α,β-unsaturated ketones. The reactive halides included activated alkyl bromides and saturated alkyl iodides. The use of the corresponding saturated alkyl bromides gave poor yields of the alkylation products.

The method was applied to the synthesis of shogaol (**29**), the pungent principle component of ginger (Scheme 6).[19] 2-Methoxy-4-methylphenol (**26**) was converted into bromide **27** by treatment with *tert*-butyldimethylsilyl chloride followed by bromination. Bromide **27** was subjected to the alkylation–Wittig reaction sequence with **7** and hexanal in a manner similar to that described above to give keto ester **28** after hydrolysis. Treatment of **28** with trifluoroacetic acid and subsequent decarboxylation gave shogaol (**29**) in 44% overall yield from **27**.

Conclusion

We have demonstrated that (2-ethoxyallylidene)triphenylphosphorane **6** undergoes [3 + 2] annulation reactions with α-bromo ketones under extremely mild conditions to give 2-ethoxycyclopentadienes in moderate to good yields and in a regioselective fashion. Subsequent mild acid treatment of the ethoxycyclopentadienes provides a new route to substituted cyclopentenones. In addition, we developed a new method for the synthesis of α,β-unsaturated ketones via an alkylation–Wittig reaction sequence on (ethoxyallylidene)triphenylphosphorane **7**.

Experimental Section

General Methods. Melting points were obtained on a hot stage apparatus and are uncorrected. The NMR spectra of all compounds were recorded in $CDCl_3$. 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 and DMF were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. Anhydrous Cs_2CO_3 supplied by Aldrich was used.

(*E*)-(2-Ethoxy-3-(ethoxycarbonyl)-2-propenyl)triphenylphosphonium Bromide (4). Ethyl 4-bromo-3-ethoxy-2-butenoate (60.0 g, 0.253 mol), prepared from ethyl 3-ethoxy-2-butenoate (**2**) according to the literature method,[20] was treated with triphenylphosphine (66.4 g, 0.253 mol) in dry benzene (300 mL) for 46 h at rt. The precipitate was collected by filtration and washed with benzene. Recrystallization from acetonitrile–ethyl acetate gave colorless crystals (98.5 g, 78%): mp 137.5–139.5 °C (dec); IR (KBr) 1680, 1610 cm^{-1}; ^1H NMR (90 MHz) δ 7.62–7.91 (m, 15 H), 5.64 (bd, J = 15.4 Hz, 2 H), 5.05 (d, J = 2.4 Hz, 1 H), 3.98 (q, J = 7.2 Hz, 2 H), 3.67 (q, J = 7.2 Hz, 2 H), 1.16 (t, J = 7.1 Hz, 3 H), 1.04 (t, J = 7.0 Hz, 3 H); MS (FAB) m/z 419 (M^+ – Br). Anal. Calcd for $C_{26}H_{28}BrO_3P$: H, 5.65; C, 62.53: P, 6.20: Br, 16.00. Found: H, 5.62; C, 62.57; P, 6.06; Br, 15.98.

(*E*)-(2-Ethoxy-3-(ethoxycarbonyl)-2-propenylidene)triphenylphosphorane (6). A solution of NaOH (2.64 g, 0.066 mol) in water (150 mL) was added dropwise to a stirred, ice-cooled solution of **4** (30.0 g, 0.060 mol) in water (700 mL). The precipitate was collected by filtration, washed with water, and dried at 60 °C in vacuo to yield yellow crystals (24.6 g, 98%): mp 166–167 °C (lit.[4f] mp 166 °C); IR (KBr) 1660 cm^{-1}; ^1H NMR (90 MHz) δ 7.24–7.85 (m, 15 H), 4.88 (bd, J = 22.9 Hz, 1 H), 4.39 (d, J = 6.6 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2 H), 3.68 (q, J = 7.0 Hz, 2 H), 1.26 (t, J = 7.0 Hz, 3 H), 0.57 (t, J = 7.0 Hz, 3 H).

(*E*)-(2-Ethoxy-3-(*tert*-butoxycarbonyl)-2-propenylidene)triphenylphosphorane (7). *tert*-Butyl 4-bromo-3-ethoxy-2-butenoate (bp 91–92 °C/0.6 mmHg, 29.7 g, 0.112 mol), prepared from *tert*-butyl 3-ethoxy-2-butenoate,[21] was treated with triphenylphosphine (30 g, 0.114 mol) as described for **4**. After evaporation of the solvent, the resulting crude phosphonium bromide syrup was dissolved in water (2 L) and filtered. The filtrate was adjusted to pH 12 with aqueous NaOH solution (1 M). The precipitates were collected by filtration, washed with

(19) For the isolation and the structure determination of shogaol, see: Nomura, H. *J. Chem. Soc.* **1917**, 769; *Sci. Rep. Tohoku Imp. Univ.* **1918**, *7*, 67; **1925**, *14*, 131. Connell, D. W.; Sutherland, M. D. *Aust. J. Chem.* **1969**, *22*, 1033.

(20) Kochhar, K. S.; Pinnich, H. W. *J. Org. Chem.* **1984**, *49*, 3222.

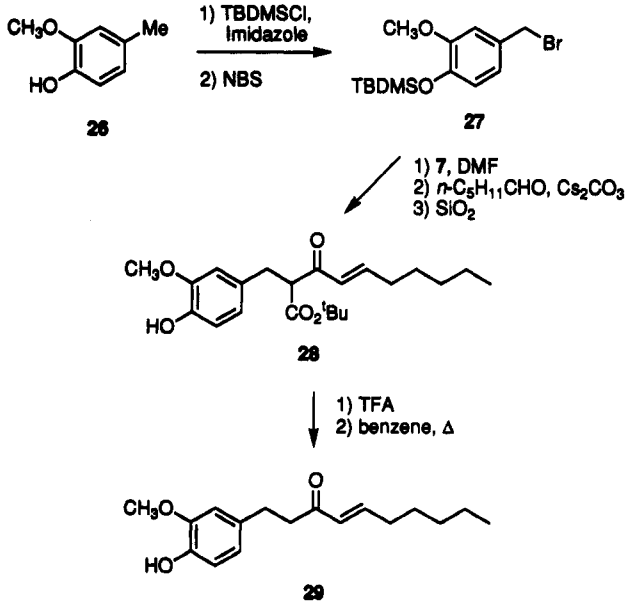
(21) Brynes, S. D.; Feder, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 7016.

Table 3. Synthesis of α,β-Unsaturated Ketones from 7

entry	reagent R¹X	reagent R²CHO	keto ester no.	keto ester yield,[a] %	α,β-unsaturated ketone no.	α,β-unsaturated ketone yield,[b] %
1	$PhCH_2Br$	PhCHO	**24a**		**20**	85[c]
2	$PhCH_2Br$	n-$C_5H_{11}CHO$	**24b**	70	**21**	99
3	n-$C_5H_{11}I$	PhCHO	**24c**	69	**25c**	100
4	n-$C_5H_{11}I$	n-$C_5H_{11}CHO$	**24d**	67	**25d**	94
5	C_2H_5I	n-$C_5H_{11}CHO$	**24e**	61	**25e**	81
6	$CH_3O_2CCH_2Br$	n-$C_5H_{11}CHO$	**24f**	68	**25f**	88

[a] Isolated yield based on the amount of phorphorane 7. [b] Isolated yield based on the amount of 24. [c] Overall yield from 7.

Scheme 6



water, and dried in vacuo. Recrystallization from dichloromethane–ethyl acetate gave yellow crystals (34.2 g, 68%): mp 173–174 °C; IR (KBr) 1650, 1500 cm^{-1}; ^1H NMR (360 MHz) δ 7.30–7.70 (m, 15 H), 4.61 (bd, J = 24.0 Hz, 1 H), 4.33 (d, J = 6.75 Hz, 1 H,), 3.66 (q, J = 7.02 Hz, 2 H), 1.50 (s, 9 H), 0.51 (t, J = 7.02 Hz, 3 H); MS (FAB) m/z 447 (M^+). 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.

Representative Procedures for the Preparation of Cyclopentadienes. Method A (from 6). A mixture of 6 (419 mg, 1 mmol), halide (1 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) in dichloromethane (20 mL) was stirred at 30 °C under nitrogen. The mixture was filtered, and the filtrate was evaporated in vacuo. The residue was passed through a short column of silica gel to remove triphenylphosphine oxide and further purified by flash chromatography (ethyl acetate:hexanes = 1:10). **Method B (2 Equiv of 6).** A mixture of 6 (838 mg, 2 mmol) and halide (1 mmol) in dichloromethane (20 mL) was stirred at 30 °C under nitrogen. After removal of the solvent, the residue was chromatographed in a manner similar to that described for method A. **Method C (from 4).** In a manner similar to that described for method A, 4 (500 mg, 1 mmol) and halide (1 mmol) were allowed to react in the presence of i-Pr_2EtN (0.5 mL, 2.3 mmol) in dichloromethane (10 mL).

These general procedures were used for the cyclopentadienes; time and yields are presented in Table 2. Physical properties were as follows:

Ethyl 2-ethoxy-4-phenyl-1,3-cyclopentadiene-1-carboxylate (9a): mp 59.5–60.5 °C (hexane–ethyl acetate); IR (Nujol) 1696, 1672, 1611, 1576 cm^{-1}; ^1H NMR (360 MHz) δ 7.60–7.31 (m, 5 H), 6.90 (bs, 1 H), 4.31 (q, J = 7.1 Hz, 2 H), 4.24 (q, J = 7.0 Hz, 2 H), 3.69 (d, J = 0.7 Hz, 2 H), 1.47 (t, J = 7.0 Hz, 3 H), 1.33 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz) δ 167.72, 164.06, 152.48, 134.55, 128.82, 128.72, 125.56, 119.88, 105.23, 67.07, 59.25, 38.13, 15.22, 14.59; MS (EI) m/z 258 (M^+); UV λ_{max} (MeOH) 342 nm (15 000). Anal. Calcd for $C_{16}H_{18}O_3$: H, 7.02; C, 74.40. Found: H, 6.95; C, 74.57.

Ethyl 2-ethoxy-4-methyl-1,3-cyclopentadiene-1-carboxylate (9b): oil; IR (neat) 1692, 1672, 1622, 1555 cm^{-1}; ^1H NMR (360 MHz) δ 6.23 (bs, 1 H), 4.20 (q, J = 7.0 Hz, 2 H), 4.18 (q, J = 7.0 Hz, 2 H), 3.18 (d, J = 0.7 Hz, 2 H), 2.10 (d, J = 1.7 Hz, 3 H), 1.41 (t, J = 7.0 Hz, 3 H), 1.28 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz) δ 168.17, 163.95, 153.86, 121.57, 103.66, 66.70, 58.90, 42.06, 17.24, 15.22, 14.59; HRMS calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1081; UV λ_{max} (MeOH) 302 (11 600), 231 nm (6100).

Ethyl 2-ethoxy-4-pentyl-1,3-cyclopentadiene-1-carboxylate (9c): oil; IR (neat) 1699, 1674, 1618, 1553 cm^{-1}; ^1H NMR (360 MHz) δ 6.23 (bs, 1 H), 4.22 (q, J = 7.0 Hz, 2 H), 4.19 (q, J = 7.0 Hz, 2 H), 3.18 (bs, 2 H), 2.40 (t, J = 7.7 Hz, 2 H), 1.54 (m, 2 H), 1.41 (t, J = 7.0 Hz, 3 H), 1.26–1.32 (m, 4 H), 1.29 (t, J = 7.0 Hz, 3 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz) δ 168.10, 164.07, 158.91, 120.47, 103.52, 66.67, 58.96, 40.40, 31.68, 31.58, 28.71, 22.48, 15.24, 14.61, 14.00; HRMS calcd for $C_{15}H_{24}O_3$ 252.1724, found 252.1709; UV λ_{max} (MeOH) 304 (5400), 237 nm (1900).

Ethyl 4-(3-chloropropyl)-2-ethoxy-1,3-cyclopentadiene-1-carboxylate (9d): mp 40–41 °C (hexane–ethyl acetate); IR (neat) 1700, 1678, 1622, 1558 cm^{-1}; ^1H NMR (360 MHz) δ 6.29 (bs, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.19 (q, J = 7.0 Hz, 2 H), 3.55 (t, J = 6.3 Hz, 2 H), 3.20 (d, J = 0.7 Hz, 2 H), 2.59 (dt, J = 1.4, 7.4 Hz, 2 H), 1.98–2.06 (m, 2H), 1.41 (t, J = 7.0 Hz, 3 H), 1.29 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz) δ 167.63, 163.92, 156.10, 121.53, 104.02, 66.98, 59.05, 44.15, 40.40, 31.61, 28.68, 15.22, 14.57; HRMS calcd for $C_{13}H_{19}ClO_2$ 258.1022, found 258.1001; UV λ_{max} (MeOH) 302 (9000), 234 nm (4100).

Ethyl 2-ethoxy-4-ethyl-5-methyl-1,3-cyclopentadiene-1-carboxylate (9e): oil; IR (neat) 1698, 1676, 1622, 1560 cm^{-1}; ^1H NMR (360 MHz) δ 6.15 (s, 1 H), 4.21 (q, J = 7.0 Hz, 2 H), 4.12–4.29 (m, 2 H), 3.19 (q, J = 7.6 Hz, 1 H), 2.37–2.46 (m, 2 H), 1.41 (t, J = 7.0 Hz, 3 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.24 (d, J = 7.6 Hz, 3 H), 1.15 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz) δ 167.61, 166.45, 164.04, 117.42, 109.65, 66.72, 58.85, 45.42, 22.66, 15.33, 15.22, 14.58, 12.68; HRMS calcd for $C_{13}H_{20}O_3$ 224.1411, found 224.1420; UV λ_{max} (MeOH) 304 nm (11300).

Ethyl 2-ethoxy-5,6,7,7a-tetrahydro-4*H*-indene-1-carboxylate (9f): oil; IR (neat) 1699, 1679, 1622, 1559 cm^{-1}; ^1H NMR (360 MHz) δ 6.13 (d, J = 1.8 Hz, 1 H), 4.13–4.26 (m, 2 H), 4.19 (q, J = 7.0 Hz, 2 H), 2.94 (dd, J = 6.2, 12 Hz, 1 H,), 2.72 (m, 1 H), 2.67 (m, 1H), 2.26 (dt, J = 5.5, 13 Hz, 1 H), 2.01 (bd, J = 13 Hz, 1 H), 1.77 (bd, J = 13 Hz, 1 H), 1.45 (m, 1 H), 1.42 (t, J = 7.0 Hz, 3 H), 1.29 (t, J = 7.0 Hz, 3 H), 1.22 (m, 1 H), 0.84 (dq, J = 3.3, 13, 1 H); ^{13}C NMR (75 MHz) δ 168.19, 163.94, 162.37, 115.69, 108.73, 66.64, 58.63, 49.31, 33.34, 29.51, 28.83, 24.56, 15.04, 14.43; HRMS calcd for $C_{14}H_{20}O_3$ 236.1411, found 236.1422; UV λ_{max} (MeOH) 305 (12 300), 237 (6800).

Ethyl 2-ethoxy-4-(ethylthio)-1,3-cyclopentadiene-1-carboxylate (9g): mp 69–70 °C (hexane–ethyl acetate); IR (Nujol) 1667, 1593, 1500 cm^{-1}; ^1H NMR (360 MHz) δ 6.18 (bs, 1 H), 4.21 (q, J = 7.0 Hz, 2 H), 4.18 (q, J = 7.0 Hz, 2 H), 3.36 (bs, 2 H), 2.91 (q, J = 7.4 Hz, 2 H), 1.41 (t, J = 7.0 Hz, 3 H), 1.37 (t, J = 7.4 Hz, 3 H), 1.28 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz) δ 167.61, 163.47, 153.28, 117.15, 102.82, 67.07, 59.05, 40.90, 26.47, 15.18, 14.58, 13.77; MS (EI) m/z 242 (M^+); UV λ_{max} (MeOH) 338 (12 500), 232 nm (10 100). Anal. Calcd for $C_{12}H_{18}O_3S$: H, 7.49; C, 59.48; S, 13.23. Found: H, 7.34; C, 59.21; S, 13.04.

Isolation of Intermediate 11. A solution of 6 (420 mg, 1 mmol) and phenacyl bromide (200 mg, 1 mmol) in $CHCl_3$ (20 mL) was stirred for 12 h at rt. The reaction mixture was separated by preparative HPLC on a GPC column ($CHCl_3$) to give 11 (191 mg, 31%), 4 (65 mg, 13%), 9a (49 mg, 19%), phenacyl bromide

(44 mg, 22% recovery), and triphenylphosphine oxide (50 mg, 31%). Compound 11: mp 160–161 °C dec (dichloromethane–ethyl acetate); IR (Nujol) 1753, 1688, 1582 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.99–7.41 (m, 20 H), 5.79 (bd, J = 9.9 Hz, 1 H), 4.68–4.80 (m, 1 H), 4.51–4.63 (m, 1 H), 4.14 (q, J = 6.9 Hz, 2 H), 3.63 (bs, 1 H), 3.60 (ABq, J = 9.9 Hz, separation of inner lines 14.8 Hz, 1 H), 2.64 (ABq, J = 8.9 Hz, separation of inner lines 16.8 Hz, 1 H), 1.43 (t, J = 6.9 Hz, 3 H), 1.26 (t, J = 6.9 Hz, 3 H). Anal. Calcd for $C_{34}H_{34}BrO_4P$: C, 66.13; H, 5.55; Br, 12.94; P, 5.02. Found: C, 66.09; H, 5.68; Br, 12.88; P, 5.11.

Ethyl 6-(4-Chlorophenyl)-3-ethoxy-6-oxo-2,4-hexadienoate (15). By means of method B, 4-chlorophenacyl bromide (233 mg, 1.0 mmol) was allowed to react with 7 (836 mg, 2.0 mmol). Flash chromatography of the crude product gave 4-(4-chlorophenyl)-2-ethoxy-1,3-cyclopentadiene-1-carboxylate (222 mg, 76%) and 15 (11 mg, 3%).

The cyclopentadiene: mp 100.5–101.5 °C (hexane); IR (KBr) 1665, 1620 cm^{-1}; ^{1}H NMR (360 MHz) δ 7.51–7.48 (m, 2 H), 7.35–7.32 (m, 2 H), 6.88 (s, 1 H), 4.31 (q, J = 7.0 Hz, 2 H), 4.24 (q, J = 7.0 Hz, 2 H), 3.65 (d, J = 0.7 Hz, 2 H), 1.46 (t, J = 7.0 Hz, 3 H), 1.33 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (90 MHz) δ 167.4, 163.9, 150.9, 134.5, 133.1, 129.0, 126.8, 120.5, 105.6, 67.1, 59.3, 38.2, 15.2, 14.5; UV (MeOH) λ_{max} 346 (ϵ 18 000), 277 (ϵ 5700), 242 (ϵ 15 000) nm; MS (EI) m/z 292 (M$^+$). Anal. Calcd for $C_{16}H_{17}ClO_3$: C, 65.64; H, 5.85; Cl, 12.11. Found: C, 65.73; H, 6.16; Cl, 12.20.

15: mp 118.5–119.5 °C (hexane); IR (KBr) 1705, 1625, 1595, 1580 cm^{-1}; ^{1}H NMR (360 MHz) δ 8.42 (d, J = 15.4 Hz, 1 H,), 7.92–7.89 (m, 2 H), 7.48–7.44 (m, 2 H), 7.40 (d, J = 15.4 Hz, 1 H), 5.34 (s, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 3.97 (q, J = 7.0 Hz, 2 H), 1.45 (t, J = 6.8 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (90 MHz) 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; UV (MeOH) λ_{max} 306 (ϵ 17 000), 226 (ϵ 15 000) nm; 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.

Representative Procedure for the Preparation of Cyclopentenone 10. Cyclopentadiene 9 (1 mmol) was dissolved in $CHCl_3$ (20 mL) and layered with aqueous HCl (2 M, 20 mL). The mixture was stirred for 12 h at rt. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed with aqueous $NaHCO_3$, dried, and evaporated in vacuo. The crude product was purified by flash chromatography (ethyl acetate: hexanes = 1:10).

This general procedure was used for the cyclopentenones. Ethyl 4-methyl-2-oxo-3-cyclopentene-1-carboxylate (**10b**) showed spectral data identical to those reported.[22] Physical properties of new compounds were as follows:

Ethyl 2-oxo-4-phenyl-3-cyclopentene-1-carboxylate (10a): oil; IR (neat) 1737, 1701, 1600, 1570 cm^{-1}; ^{1}H NMR (360 MHz) δ 7.44–7.69 (m, 5H), 6.53 (dd, J = 1.5, 1.5 Hz, 1 H), 4.25 (q, J = 7.0 Hz, 2 H), 3.62 (dd, J = 7.4, 3.0 Hz, 1 H), 3.48 (ddd, J = 1.5, 3.0, 18 Hz, 1 H), 3.25 (ddd, J = 1.5, 7.4, 18 Hz, 1 H), 1.32 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz) δ 201.38, 173.48, 168.92, 133.23, 131.67, 128.92, 126.96, 125.19, 61.63, 52.19, 32.60, 14.13; HRMS calcd for $C_{14}H_{14}O_3$ 230.0942, found 230.0931.

Ethyl 2-oxo-4-pentyl-3-cyclopentene-1-carboxylate (10c): oil; IR (neat) 1736, 1704, 1615 cm^{-1}; ^{1}H NMR (360 MHz) δ 5.90 (bs, 1 H), 4.21 (dq, J = 7.0, 1.0 Hz, 2 H), 3.44 (dd, J = 7.2, 2.7 Hz, 1 H), 2.98 (ddd, J = 18, 2.7, 1.0 Hz, 1 H), 2.78 (ddd, J = 18, 7.2, 1.0 Hz, 1 H), 2.45 (t, J = 7.5 Hz, 2 H), 1.62 (m, 2 H), 1.30–1.36 (m, 4 H), 1.29 (dt, J = 7.0, 1.0 Hz, 3 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (90 MHz) δ 202.16, 183.09, 169.16, 127.46, 61.58, 52.33, 35.58, 33.36, 31.46, 26.64, 22.38, 14.22, 13.91; HRMS calcd for $C_{13}H_{20}O_3$ 224.1411, found 224.1407.

Ethyl 4-(3-chloropropyl)-2-oxo-3-cyclopentene-1-carboxylate (10d): oil; IR (neat) 1737, 1704, 1620 cm^{-1}; ^{1}H NMR (360 MHz) δ 5.94 (bs, 1 H), 4.22 (q, J = 7.0 Hz, 2 H), 3.61 (t, J = 6.3 Hz, 2 H), 3.45–3.47 (m, 1 H), 2.99–3.04 (m, 1 H), 2.8 (m, 1 H), 2.64 (t, J = 7.4 Hz, 2 H), 2.10 (tt, J = 6.3, 7.4 Hz, 2 H), 1.30 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz) δ 201.65, 180.96, 168.93, 127.78, 61.60, 52.28, 44.00, 35.61, 30.44, 29.63, 14.18; HRMS calcd for $C_{11}H_{15}ClO_3$ 230.0709, found 230.0719.

(22) Hellow, J.; Kingston, J. F.; Fallis, A. G. *Synthesis* **1984**, 1014.

Ethyl 3-Ethyl-2-methyl-5-oxo-3-cyclopentene-1-carboxylate (10e). This compound was obtained in the trans form with over 95% selectivity: oil; IR (neat) 1735, 1700, 1615 cm^{-1}; ^{1}H NMR (360 MHz) δ 5.88 (bs, 1 H), 4.21 (q, J = 7.0 Hz, 2 H), 3.23 (bq, J = 7.4 Hz, 1 H), 3.04 (d, J = 3.0 Hz, 1 H), 2.30–2.55 (m, 2 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.26 (d, J = 7.4 Hz, 3 H), 1.21 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz) δ 201.11, 187.79, 169.10, 126.21, 61.51, 60.93, 42.29, 24.18, 18.01, 14.20, 11.28; HRMS calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1069.

Ethyl 2,4,5,6,7,7a-Hexahydro-2-oxo-1*H*-indene-1-carboxylate (10f). This compound was obtained in the trans form with over 95% selectivity:[23] oil; IR (neat) 1735, 1710, 1624 cm^{-1}; ^{1}H NMR (360 MHz) δ 5.81 (s, 1 H), 4.22 (q, J = 7.0 Hz, 2 H), 3.43 (dd, J = 4, 13 Hz, 1 H), 3.02 (bs, 1 H), 2.85 (bd, J = 13 Hz, 1 H), 2.29 (dt, J = 13, 3 Hz, 1 H), 2.25 (m, 1 H), 2.03 (m, 1 H), 1.88 (bd, J = 13 Hz, 1 H), 1.54 (tq, J = 3, 13 Hz, 1 H), 1.39 (tq, J = 3, 13 Hz, 1 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.20 (dq, J = 3, 13 Hz, 1 H); ^{13}C NMR (75 MHz) δ 201.34, 184.22, 169.23, 124.97, 61.48, 59.33, 45.94, 34.02, 30.89, 26.60, 25.03, 14.20; HRMS calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1067.

Ethyl 4-(ethylthio)-2-oxo-3-cyclopentene-1-carboxylate (10g): oil; IR (neat) 1735, 1694, 1549 cm^{-1}; ^{1}H NMR (360 MHz) δ 5.88 (bs, 1 H), 4.23 (q, J = 7.2 Hz, 2 H), 3.52 (dd, J = 7.5, 3.1 Hz, 1 H), 3.19 (ddd, J = 17.6, 3.1, 1,6 Hz, 1 H), 2.96 (q, J = 7.5 Hz, 2 H), 2.95 (bd, J = 17.6 Hz, 1 H), 1.40 (t, J = 7.5 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz) δ 197.69, 180.25, 168.91, 121.52, 61.74, 52.12, 35.44, 27.14, 14.20, 13.31; HRMS calcd for $C_{10}H_{14}O_3S$ 214.0663, found 214.0652.

Ethyl 2-Benzyl-3-ethoxy-5-phenyl-2,4-pentadienoate (18a). To a stirred solution of 6 (836 mg, 2 mmol) in DMF (4 mL) was added benzyl bromide (0.25 mL, 2.1 mmol) under Ar, and the mixture was stirred for 48 h at rt. t-BuOK (1 M in THF, 2.0 mL) was added to the solution. After 1 h, benzaldehyde (0.22 mL, 2.1 mmol) was added, and the mixture was warmed at 60 °C for 24 h. After cooling, the mixture was poured into ice–water (20 mL) and extracted with ethyl acetate. The extract was washed with brine, dried, and evaporated in vacuo. The residue was passed through a short column of silica gel to remove triphenylphosphine oxide and further purified by flash chromatography (ether: hexanes = 3:1) to give (2*E*,4*E*)-**18a** (446 mg, 66%) and (2*Z*,4*E*)-**18a** (125 mg, 18.5%).

(2*E*,4*E*)-**18a**: oil; IR (neat) 1695, 1620, 1580 cm^{-1}; ^{1}H NMR (360 MHz) δ 7.71 (d, J = 16.1 Hz, 1 H), 7.15–7.52 (m, 10 H), 7.01 (d, J = 16.1 Hz, 1 H), 4.13 (q, J = 7.0 Hz, 2 H), 3.91 (q, J = 7.0 Hz, 2 H), 3.89 (s, 2 H), 1.37 (t, J = 7.0 Hz, 3 H), 1.18 (t, J = 7.0 Hz, 3 H); UV (MeOH) λ_{max} 314 nm (19,000), 234 nm (8,700); HRMS calcd for $C_{22}H_{24}O_3$ 336.1724, found 336.1691.

(2*Z*,4*E*)-**18a**: oil; IR (neat) 1700, 1610, 1580 cm^{-1}; ^{1}H NMR (360 MHz) δ 7.41–7.44 (m, 2 H), 7.16–7.36 (m, 8 H), 7.12 (d, J = 15.8 Hz, 1 H), 6.91 (d, J = 15.8 Hz, 1 H), 4.17 (q, J = 7.0 Hz, 2 H), 3.99 (q, J = 7.0 Hz, 2 H), 3.82 (s, 2 H), 1.40 (t, J = 7.0 Hz, 3 H), 1.22 (t, J = 7.0 Hz, 3 H); UV (MeOH) λ_{max} 312 nm (29 000), 229 nm (11 000); HRMS calcd for $C_{22}H_{24}O_3$ 336.1724, found 336.1718.

Ethyl (*E*)-2-Benzyl-3-oxo-5-phenyl-4-pentenoate (19a). A suspension of silica gel (Wako gel C-200, 300 mg) in dichloromethane (1 mL) was treated with two drops of aqueous 15% sulfuric acid. To the suspension was added (2*E*,4*E*)-**18a** (103 mg, 0.306 mmol), and the mixture was stirred for 64 h at rt until TLC showed complete disappearance of the starting material. The mixture was treated with $NaHCO_3$ (30 mg) and filtered. The solid was washed well with dichloromethane, and the organic layers were dried and evaporated in vacuo. The crude product was purified by flash chromatography (ethyl acetate:hexanes = 1:20) to yield an oil (89 mg, 95%) as a mixture of the keto–enol tautomers. Recrystallization from hexane gave colorless needles of enol **19a**: mp 79–81 °C; IR (KBr) 1730, 1640, 1620 cm^{-1}; ^{1}H NMR (90 MHz) δ 12.92 (d, J = 1.5 Hz, 1 H), 7.12–7.55 (m, 10 H), 6.96 (dd, J = 2.0, 15.8 Hz, 1 H), 7.54 (d, J = 15.8 Hz, 1 H), 4.18 (q, J = 7.1 Hz, 2 H), 3.77 (s, 2 H), 1.23 (t, J = 7.1 Hz, 3 H);. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.86; H, 6.48.

(23) The preparation of this compound as a cis and trans mixture has been reported: Corey, E. J.; Ghosh, A. K. *Tetrahedron Lett.* **1987**, *28*, 175.

By means of the same procedure, (2Z,4E)-**18a** (200 mg, 0.59 mmol) was converted into **19a** (155 mg, 89%) as a mixture of the keto–enol isomers.

Ethyl (*E*)-2-Benzyl-3-oxo-4-decenoate (19b). By means of the procedure described for **18a**, **6** (2.09 g, 5.0 mmol) was allowed to react with benzyl bromide (0.613 mL, 5.1 mmol) and then hexanal (0.6 mL, 5.0 mmol). Flash chromatography of the crude product gave **18b** (1.36 g, 83%) as an oily mixture of the geometrical isomers. Enol ether **18b** (400 mg, 1.21 mmol) was treated with a suspension of silica gel (4 g) and aqueous 15% sulfuric acid (0.08 mL) in dichloromethane (10 mL) by means of the procedure described for **19a** to yield **19b** as an oil (355 mg, 97%): IR (neat) 1740, 1690, 1650, 1630 cm^{-1}; ^1H NMR (90 MHz) δ 7.10–7.42 (m, 5 H), 6.91 (dt, J = 15.8, 6.8 Hz, 1 H), 6.16 (dt, J = 15.8, 1.4 Hz, 1 H), 4.12 (q, J =7.1 Hz, 2 H), 3.98 (t, J = 7.5 Hz, 1 H), 3.19 (d, J = 7.5 Hz, 2 H), 2.06–2.15 (m, 2 H), 1.00–1.62 (m, 9 H), 0.77–1.00 (m, 3 H); MS (EI) m/z 302 (M^+). Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.25; H, 8.55.

(*E*)-1,5-Diphenyl-1-penten-3-one (20) from Ethyl (*E*)-2-Benzyl-3-oxo-5-phenyl-4-pentenoate (19a). A mixture of **19a** (50 mg, 0.61 mmol), sodium chloride (15 mg), and water (0.001 mL) in DMSO (0.1 mL) was heated at 140 °C for 12 h. After cooling, the mixture was poured into water (10 mL) and extracted with ether. The extract was washed with brine, dried, and evaporated in vacuo. Flash chromatography of the crude product gave crystals (20 mg, 52%): mp 54–56 °C (pentane); IR (KBr) 1685, 1660, 1610 cm^{-1}; ^1H NMR (270 MHz) δ 7.54 (d, J = 16.2 Hz, 1 H), 7.18–7.55 (m, 12 H), 6.73 (d, J = 16.2 Hz, 1 H), 3.00 (s, 4 H); ^{13}C NMR (67.5 MHz) δ 199.2, 142.6, 141.2, 134.4, 130.4, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 126.1, 126.0, 42.4, 30.1. Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.28; H, 6.71.

(*E*)-1-Phenyl-4-decen-3-one (21) from Ethyl (*E*)-2-Benzyl-3-oxo-4-decenoate (19b). By means of the procedure described for **20**, **19b** (200 mg, 0.66 mmol) was decarboxylated. Flash chromatography of the crude product gave **21** (61 mg, 40%) and 1-phenyl-5-decen-3-one **22** (20 mg, 13%).

21: oil; IR (liquid film) 1690, 1665, 1625 cm^{-1}; ^1H NMR (270 MHz) δ 7.05–7.31 (m, 5 H), 6.82 (dt, J = 15.8, 6.9 Hz, 1 H), 6.09 (dd, J = 15.8, 1.7 Hz, 1 H), 2.83–2.98 (m, 4 H), 2.15–2.23 (m, 2 H), 1.38–1.50 (m, 2 H), 1.20–1.38 (m, 4 H), 0.88 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (67.5 MHz) δ 199.5, 147.8, 141.3, 130.2, 130.1, 128.4, 128.3, 126.0, 41.6, 32.4, 31.3, 30.1, 27.7, 22.4, 13.9. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.18; H, 9.34.

22: oil; IR (liquid film) 1700 cm^{-1}; ^1H NMR (90 MHz) δ 7.07–7.39 (m, 5 H), 5.44–5.58 (m, 2 H), 2.30–2.60 (m, 6 H), 1.83–2.19 (m, 2 H), 1.04–1.44 (m, 4 H), 0.76–1.04 (m, 3 H); MS (EI) m/z 230 (M^+). Compound **22** was transformed into **21** upon treatment with a trace of HCl in a $CDCl_3$ solution.

Representative Procedure for the Preparation of β-Keto Esters from (4-(*tert*-Butoxycarbonyl)-2-ethoxy-2-propenylidene)triphenylphosphorane (7). By means of the procedure described for **18a**, **7** (447 mg, 1 mmol) was allowed to react with the halide (1.1 mmol) and then the aldehyde (1.0 mmol) with Cs_2CO_3 (326 mg, 1.0 mmol) as a base instead of t-BuOK. The residue was passed through a short column of silica gel to remove triphenylphosphine oxide. The resulting crude enol ether was hydrolyzed with silica gel in a manner similar to that described for **19a**.

This general procedure was used for the β-keto esters; yields are presented in Table 3. Physical properties were as follows:

***tert*-Butyl (*E*)-2-Benzyl-3-oxo-4-decenoate (24b).** This compound was obtained as a 6:1 mixture of the keto and enol forms: oil; IR (neat) 1725, 1690, 1670, 1620 cm^{-1}; ^1H NMR (270 MHz) δ 13.00 (s, 1 × 1/7 H, enol H), 7.05–7.50 (m, 5 H), 6.91 (dt, J = 15.8, 6.9 Hz, 1 H), 6.18 (d, J = 15.8 Hz, 1 H), 3.89 (t, J = 7.0 Hz, 1 × 6/7 H), 3.59 (s, 2 × 1/7 H), 3.15 (d, J = 7.0 Hz, 2 × 6/7 H), 2.18 (m, 2 H), 1.36 (s, 9 H), 1.09–1.50 (m, 6 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (67.5 MHz) for the major keto form δ 194.0, 168.4, 149.5, 138.6, 128.9, 128.3, 126.4, 81.7, 59.4, 34.0, 32.5, 31.2, 27.8, 27.6, 22.3, 13.9; MS (EI) m/z 330 (M^+). Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.33; H, 9.15. Found: C, 76.58; H, 9.03.

***tert*-Butyl (*E*)-3-Oxo-2-pentyl-5-phenyl-4-pentenoate (24c).** This compound was obtained as a 5:1 mixture of the keto and enol tautomers: oil; IR (neat) 1730, 1690, 1665, 1610 cm^{-1}; ^1H NMR (270 MHz) δ 12.90 (s, 1 × 1/6 H, enol H), 7.66 (d, J = 16.2 Hz, 1 H), 7.33–7.58 (m, 5 H), 6.87 (d, J = 16.2 Hz, 1 H), 3.61 (t, J = 7.5 Hz, 1 × 5/6 H), 1.78–1.99 (m, 2 H), 1.53 (s, 1 × 1/6 H), 1.44 (s, 9 × 5/6 H), 1.30–1.38 (m, 6 H), 0.88 (m, 3 H); ^{13}C NMR (67.5 MHz) δ 194.8, 169.3, 143.6, 134.4, 130.6, 128.9, 128.4, 124.2, 81.6, 58.9, 31.6, 28.3, 27.9, 27.0, 22.4, 13.9; MS (EI) m/z 316 (M^+). Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.85; H, 8.69.

***t*-Butyl (*E*)-3-Oxo-2-pentyl-4-decenoate (24d):** oil; IR (neat) 1730, 1695, 1680, 1630 cm^{-1}; ^1H NMR (270 MHz) δ 6.94 (dt, J = 15.8 Hz, 6.9 Hz, 1 H), 6.19 (dt, J = 15.8 Hz, 1.5 Hz, 1 H), 3.51 (t, J = 7.4 Hz, 1 H), 2.18–2.26 (m, 2 H), 1.70–1.93 (m, 2 H), 1.43 (s, 9 H), 1.28–1.50 (m, 12 H), 0.87 (m, 6 H); ^{13}C NMR (67.5 MHz) δ 169.3, 148.9, 128.3, 81.4, 58.0, 32.5, 32.2, 31.3, 28.1, 27.8, 27.7, 26.9, 22.4, 13.9; MS (EI) m/z 310 (M^+). Anal. Calcd for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04. Found: C, 73.28; H, 10.98.

***tert*-Butyl (*E*)-2-ethyl-3-oxo-4-decenoate (24e):** oil; IR (neat) 1735, 1700, 1680, 1630 cm^{-1}; ^1H NMR (270 MHz) δ 6.95 (dt, J = 15.8, 6.9 Hz, 1 H), 6.21 (dt, J = 15.8, 1.3 Hz, 1 H), 3.44 (t, J = 7.4 Hz, 1 H), 2.21–2.24 (m, 2 H), 1.83–1.90 (m, 2 H), 1.43 (s, 9 H), 1.30–1.51 (m, 6 H), 0.91 (m, 6 H); ^{13}C NMR (67.5 MHz) δ 194.8, 169.2, 148.9, 128.4, 81.4, 59.6, 32.5, 31.3, 27.9, 27.7, 22.4, 21.6, 13.9, 11.8. Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found: C, 71.36; H, 10.37.

Methyl (*E*)-3-(*tert*-butoxycarbonyl)-4-oxo-5-undecenoate (24f): oil; IR (neat) 1735, 1690, 1680, 1630 cm^{-1}; ^1H NMR (270 MHz) δ 7.01 (dt, J = 15.8 Hz, 6.9 Hz, 1 H), 6.29 (d, J = 15.5 Hz, 1 H), 4.11 (t, J = 7.3 Hz, 1 H,), 3.68 (s, 3 H), 2.88 (d, J = 7.3 Hz, 2 H), 2.20–2.29 (m, 2 H), 1.43 (s, 9 H), 1.26–1.55 (m, 6 H), 0.90 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (67.5 MHz) δ 193.2, 172.0, 167.7, 149.9, 128.5, 82.3, 53.2, 51.9, 32.5, 32.2, 31.3, 27.8, 27.6, 22.4, 13.9. Anal. Calcd for $C_{17}H_{28}O_5$: C, 65.36; H, 9.03. Found: C, 65.51; H, 9.01.

Representative Procedure for the Preparation of α,β-Unsaturated Ketone from Keto Ester 24. Keto ester **24** (1.0 mmol) was dissolved in trifluoroacetic acid (1.0 mL) at 0 °C, and the solution was stirred for 1 h at rt. The mixture was diluted with dry benzene (20mL) and evaporated in vacuo. The residue was dissolved in dry benzene (20 mL) and evaporated in vacuo. The operation was repeated twice to remove the trifluoroacetic acid. The resulting crude acid was heated in refluxing benzene for 1 h. The solution was evaporated, and the crude product was purified by flash chromatography (ether:hexanes = 1:3).

This general procedure was used for the majority of the α,β-unsaturated ketones; yields are presented in Table 3. (*E*)-1,5-Diphenyl-2-penten-3-one (**20**) and (*E*)-1-phenyl-4-decen-3-one (**21**) were identical with those obtained from the corresponding ethyl ester. (*E*)-5-Undecen-4-one (**25e**) showed spectral data identical with those reported.[24]

(*E*)-1,5-Diphenyl-1-penten-3-one (20). Compound **20** was prepared from **7** (447 mg, 1.0 mmol), benzyl bromide (0.133 mL, 1.1 mmol), and benzaldehyde (0.119 mL, 1.1 mmol) by means of the representative procedure for the preparation of keto esters. The resulting *tert*-butyl (*E*)-2-benzyl-3-oxo-5-phenyl-4-pentenoate (**24a**) was accompanied by **20**, and,hence, the crude product was treated with trifluoroacetic acid to yield **20** (188 mg, 80% from **7**).

(*E*)-1-Phenyl-1-nonen-3-one (25c): oil; IR (neat) 1690, 1660, 1610 cm^{-1}; ^1H NMR (270 MHz) δ 7.38–7.58 (m, 6 H), 6.74 (d, J = 16.2 Hz, 1 H), 2.65 (t, J = 7.4 Hz, 2 H), 1.60–1.73 (m, 2 H), 1.26–1.45 (m, 6 H), 0.89 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (67.5 MHz) δ 200.5, 142.2, 134.6, 130.3, 128.8, 128.2, 126.2, 40.9, 31.6, 28.9, 24.3, 22.4, 14.0; MS (EI) m/z 316 (M^+). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.34; H, 9.01.

(*E*)-6-Tetradecen-8-one (25d): oil; IR (neat) 1690, 1670, 1625 cm^{-1}; ^1H NMR (270 MHz) δ 6.82 (dt, J = 15.8, 6.9 Hz, 1 H), 6.08 (d, J = 15.8 Hz, 1 H), 2.52 (t, J = 7.4 Hz, 2 H), 2.16–2.35 (m, 2 H), 1.55–1.70 (m, 2 H), 1.40–1.55 (m, 2 H), 1.26–1.40 (m, 10 H), 0.86–0.92 (m, 6 H); ^{13}C NMR (67.5 MHz) δ 201.2, 147.5, 130.6, 40.4, 32.7, 31.9, 31.6, 29.3, 28.1, 24.6, 22.8, 22.7, 14.3, 14.2; MS (EI) m/z 210 (M^+). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 80.16; H, 12.22.

Methyl (*E*)-4-oxo-5-undecenoate (25f): oil; IR (neat) 1740, 1695, 1675, 1630 cm^{-1}; ^1H NMR (270 MHz) δ 6.89 (dt, J = 15.8,

(24) Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258.

6.9 Hz, 1 H), 6.19 (d, J = 15.8 Hz, 1 H), 3.68 (s, 3 H), 2.89 (t, J = 7.6 Hz, 2 H), 2.63 (t, J = 7.6 Hz, 2 H), 2.18–2.26 (m, 2 H), 1.40–1.54 (m, 2 H), 1.26–1.40 (m, 4 H), 0.90 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (67.5 MHz) δ 198.1, 173.4, 148.1, 129.9, 51.8, 34.4, 32.4, 31.3, 27.8, 27.7, 22.4, 13.9; MS (EI) m/z 212 (M^+). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.62; H, 9.32.

3-(*tert*-Butyldimethylsiloxy)-2-methoxybenzyl Bromide (27). To a solution of 2-methoxy-4-methylphenol (**26**, 5.0 g, 36.2 mmol) and imidazole (4.93 g, 72.4 mmol) in DMF (50 mL) was added *tert*-butyldimethylsilyl chloride (6.0 g, 39.8 mmol), and the mixture was stirred for 2.5 h at rt. The mixture was poured into aqueous $NaHCO_3$ solution and extracted with hexane. The extract was washed with water, dried, and evaporated in vacuo. The residue was distilled under reduced pressure to give 4-(*tert*-butyldimethylsiloxy)-3-methoxytoluene (9.13 g, 93%), bp 87–88 °C/0.25 mmHg. A mixture of the resulting oil (7.5 g, 29.7 mmol), NBS (5.29 g, 29.7 mmol), and benzoyl peroxide (0.72 g, 0.3 mmol) in carbon tetrachloride (30 mL) was refluxed for 3 h under N_2. After cooling, the mixture was filtered, and the filtrate was washed with saturated aqueous $NaHCO_3$ solution and water, dried, and evaporated in vacuo. The residue was distilled under reduced pressure to give a pale yellow oil (8.23 g, 84%): bp 117–118 °C/0.3 mmHg; ^{1}H NMR (90 MHz) δ 6.80–6.89 (m, 3 H), 4.48 (s, 2 H), 3.81 (s, 3 H), 0.99 (s, 9 H), 0.15 (s, 6 H). This compound was unstable and was used in the next step immediately after distillation.

***tert*-Butyl (*E*)-2-((4-Hydroxy-3-methoxyphenyl)methyl])-3-oxo-4-decenoate (28).** By means of the representative procedure described for **24**, compound **28** was prepared from **7** (447 mg, 1.0 mmol), **27** (398 mg, 1.2 mmol), and hexanal (0.14 mL, 1.1 mmol) as a pale yellow oil (183 mg, 49% based on **7**): IR (neat) 1730, 1690, 1670, 1630 cm^{-1}; ^{1}H NMR (270 MHz) δ 6.91 (dt, J = 15.8 Hz, 6.9 Hz, 1 H), 6.66–6.82 (m, 3 H), 6.18 (dt, J = 15.8, 1.4 Hz, 1 H), 5.46 (s, 1 H), 3.85 (s, 3 H), 3.84 (t, J = 7.4 Hz, 1 H), 3.08 (dd, J = 1.5, 7.4 Hz, 2 H), 2.15–2.24 (m, 2 H), 1.38 (s, 9 H), 1.22–1.55 (m, 6 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (67.5 MHz) δ 194.2, 168.5, 149.5, 146.2, 144.3, 130.5, 128.7, 121.5, 114.2, 111.6, 81.7, 59.8, 55.9, 33.8, 32.5, 31.3, 27.8, 27.7, 22.4, 13.9 HRMS calcd for $C_{22}H_{32}O_5$ 376.2248, found 376.2217.

(*E*)-1-(4-Hydroxy-3-methoxyphenyl)-4-decen-3-one (Shogaol) (29). By means of the representative procedure described for **25**, compound **29** was prepared from **28** (50 mg, 0.133 mmol) as a pale yellow oil (34 mg, 92%), which showed spectral data consistent with those reported[19] for shogaol. IR (neat) 3700–3070, 1690, 1665, 1625, 1510 cm^{-1}; ^{1}H NMR (270 MHz) δ 6.67–6.87 (m, 4 H), 6.09 (dt, J = 16.2, 1.5 Hz, 1 H), 5.47 (bs, 1 H), 3.87 (s, 3 H), 2.81–2.89 (m, 4 H), 2.15–2.24 (m, 2 H), 1.26–1.50 (m, 6H), 0.89 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (67.5 MHz) δ 199.9, 147.9, 146.4, 143.8, 133.2, 130.3, 120.8, 114.3, 111.1, 55.8, 41.9, 32.4, 31.3, 29.8, 27.7, 22.4, 13.9; MS (EI) m/z 276 (M^+). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.00; H, 8.52.

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Supplementary Material Available: ^{1}H NMR spectra for compounds **6**, **9a–g**, **10a–g**, **18a**, **22**, **27**, and **28** and ^{13}C NMR spectra for compounds **9c**, **9e**, **9f**, **10c**, **10e**, and **10f** (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.