Cross-coupling Reaction between Enol Phosphates and Organoaluminium Compounds in the Presence of Palladium(0) Catalyst

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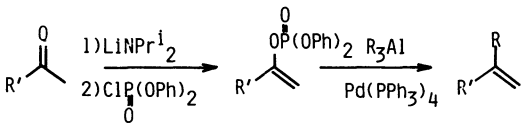
The title reaction in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) affords alkylative coupling products in good to excellent yields in 1,2-dichloroethane at room temperature. This coupling reaction under C(sp^2)-O cleavage proceeds stereospecifically. The reaction does not affect a coexisting vinyl sulfide group. This feature enables 1,2- and 1,3-carbonyl transposition with or without alkylation *via* phenylthio-substituted enol phosphates.

The regioselective transformation of ketones into alkyl-substituted olefins is an important process in organic synthesis. The classical Grignard addition to ketones or organolithium version, followed by dehydration of the resultant alcohols, generally gives isomeric olefins and/or skeletal rearrangement products.[1] We report here (1) regioselective olefin formation[2] and (2) keto carbonyl 1,2- and 1,3-transposition[3] by palladium(0)-promoted cross-coupling of enol diphenyl phosphates and organoaluminium compounds.

(1) Regioselective Olefin Formation from Ketones. During the past decade, cross-coupling of alkenyl halides with organolithium and organomagnesium compounds has been achieved in the presence of Pd(0) or Ni(0) catalyst.[4,5] However there are few examples of the replacement of an enolate oxygen by an alkyl substituent.[6] We have found that organoaluminium compounds cause alkylation of enol phosphates under the C(sp^2)-O bond fission in the presence of a catalytic amount of $Pd(PPh_3)_4$ (Scheme 1). The results are summarized in Table 1.



Scheme 1.

Alkynyl (Runs, 3, 4, 8, and 10) and alkenyl group (Run 5) were introduced selectively in preference to the ubiquitous alkyl substituents on aluminium. The reaction of (*E*)-1-heptenyldiisobutylaluminium (Run 5) prepared *in situ* from 1-heptyne and Bu^i_2AlH in hexane,[7] gave a diene having and (*E*) olefinic linkage as the sole product.

Organolithium and magnesium compounds were not suitable for this reaction, as these organometallics caused nucleophilic attack on phosphorus atom of 1-phenylethenyl diphenyl phosphate (**1**), produc-

TABLE 1. COUPLING REACTION BETWEEN ENOL DIPHENYL PHOSPHATES AND ORGANOALUMINIUM REAGENTS CATALYZED BY $Pd(PPh_3)_4$[a]

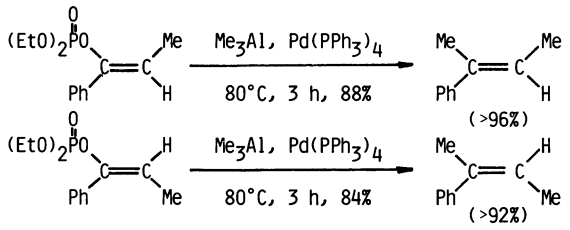
Run	Enol phosphate	Aluminium reagent	Reaction time / h	Yield[b] of coupling product / %
1	$CH_3(CH_2)_9C(OP(OPh)_2)=CH_2$	Me_3Al	2	91
2	$CH_3(CH_2)_9C(OP(OPh)_2)=CH_2$	Et_3Al	3	71
3	$CH_3(CH_2)_9C(OP(OPh)_2)=CH_2$	$PhC{\equiv}C\text{-}AlEt_2$	3	82[c]
4	$CH_3(CH_2)_9C(OP(OPh)_2)=CH_2$	$CH_3(CH_2)_3C{\equiv}C\text{-}AlEt_2$	3	59[c]
5	$CH_3(CH_2)_9C(OP(OPh)_2)=CH_2$	$CH_3(CH_2)_4CH(C{\equiv}C\text{-}AlBu^i_2)=CH_2$	4	66
6	$PhC(OP(OPh)_2)=CH_2$	Me_3Al	2	94[d]
7	$PhC(OP(OPh)_2)=CH_2$	Et_3Al	2	80
8	$PhC(OP(OPh)_2)=CH_2$	$PhC{\equiv}C\text{-}AlEt_2$	3	67[c]
9	**1**	Me_3Al	5	72
10	**1**	$PhC{\equiv}C\text{-}AlEt_2$	6	70[c]
	2			

a) Reactions were performed on 2.0 mmol scale at 25 °C. Four mmol of aluminium reagent and 0.2 mmol of $Pd(PPh_3)_4$ were employed. b) Yields are based on isolated, purified products. c) Ethylated products were not detected. The sole product was the respective 2-substituted ethynylation product. d) GLPC yield.

ing acetophenone upon workup. In contrast, the less nucleophilic organoaluminium compounds effectively induce the desired replacement of diphenyl phosphate group under new C-C bond formation.[8]

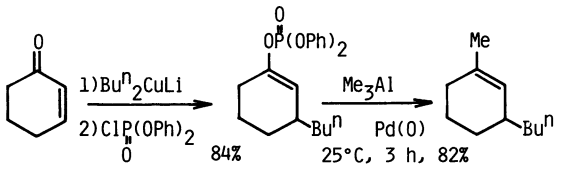
The reaction did not occur in the absence of the Pd(0) catalyst. Yields in the reaction between enol phosphate **2** and trimethylaluminium in the presence of various kinds of catalysts are given below: [Ni(acac)$_2$] (80 °C, 6 h, 12%), [Ni(acac)$_2$]-PPh$_3$-Bu$^i_2$AlH (80 °C, 6 h, 18%), [NiBr$_2$(PPh$_3$)$_2$] (80 °C, 6 h, <5%), [PdCl$_2$(PhCN)$_2$] (80 °C, 8 h, <5%), [Pd(acac)$_2$] (80 °C, 8 h, <5%).

The cross-coupling reactions proceed stereospecifically, analogously as those of alkenyl halides and organolithium compounds (or Grignard reagents).[5a] For example, methylation of (*Z*)- and (*E*)-1-phenyl-1-propenyl diethyl phosphates[9] afforded (*E*)- and (*Z*)-2-phenyl-2-butene in 88 and 84% yield; their isomeric purities are over 96 and 92% respectively (Scheme 2). The diethyl phosphate group is less effective than diphenyl phosphate as a leaving group. The reaction between diethyl phosphates and Me$_3$Al did not proceed at 25 °C but required heating at reflux in 1,2-dichloroethane.



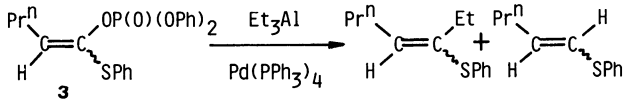
Scheme 2.

An enol phosphate was prepared alternatively by 1,4-addition of lithium dialkylcuprate(I) to an α,β-unsaturated carbonyl compound, followed by trapping of the resulting enolate with diphenyl phosphorochloridate.[10] Treatment of the enol phosphate furnished selective 1,3-dialkylation of the original conjugated enone (Scheme 3).



Scheme 3.

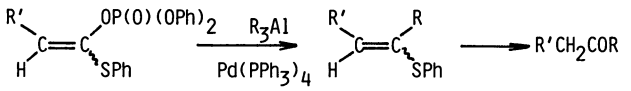
(2) 1,2- and 1,3- Transposition of a Keto Group. Scheme 4 shows that the present procedure does not affect the coexisting vinyl sulfide group, in sharp contrast to the Takei's analogous sp^2 carbon alkylation with Ni(0) catalyst.[11] Since alkenyl sulfides are valuable synthetic precursors of carbonyl compounds,[12,13] further extension of this reaction has been explored.



Scheme 4.

Treatment of phenylthio-substituted enol phosphate with organoaluminium compounds bearing a β-hydrogen, such as triethylaluminium, has afforded a mixture of the alkylated product and the hydrogenated one (Scheme 4). The ratios of these two products heavily depended on the solvents used. The reaction of the enol phosphate **3** and Et$_3$Al gave the following ratios of ethylated and hydrogenated products in solvents given in parentheses: 29:71 (hexane), 48:52 (1,2-dichloroethane), 62:38 (benzene), 71:29 (ether), 60:40 (THF), 71:29 (THF-HMPA, 9:1). The ethylated product was favored by using more

Table 2. Coupling reaction between enol phosphates derived from thiocarboxylic *S*-esters and organoaluminium reagents catalyzed by Pd(PPh$_3$)$_4$[a]



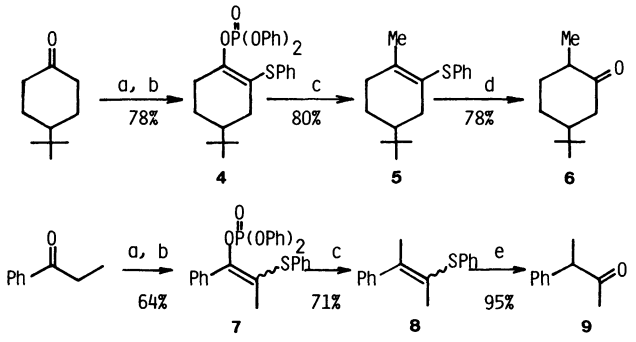
Enol phosphate R′	Aluminium reagent	Reaction time h	Yield of sulfide %	Yield of ketone %
$CH_3CH_2CH_2$	Me_3Al	1	83	70[b]
	Et_3Al	2	82[c]	—
	$PhC{\equiv}C\text{-}AlEt_2$	2	83[d]	—
	$CH_3(CH_2)_4\underset{H}{\overset{|}{C}}{=}C\text{-}AlBu^i_2$	3	62[d]	65[e]
Ph	Me_3Al	1	64	89[b]
	Et_3Al	2	55[c]	—

a) Reactions were performed on 2.0 mmol scale at 25 °C in benzene. Four mmol of aluminium reagent and 0.2 mmol of Pd(PPh$_3$)$_4$ were employed. b) Hydrolysis with TiCl$_4$. See Ref. 13. c) Mixture of ethylated and hydrogenated products in 3:2 ratio. d) Ethynylation or ethenylation product was obtained exclusively. e) Hydrolysis with HgCl$_2$. See Ref. 14.

polar solvents.

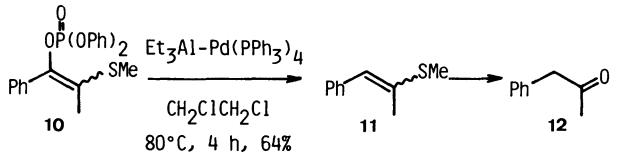
Coupling reactions between enol phosphates derived from thiocarboxylic *S*-esters and organoaluminium reagents are shown in Table 2. Hydrolysis of the resulting vinyl sulfides with $TiCl_4$[13] or $HgCl_2$[14] proceeded easily to give the corresponding ketones.

Scheme 5 provides 1,2-transposition[15] of a carbonyl group, accompanied by alkylation. Treatment of the enol phosphate **4** derived from α-phenylthio ketone with Me_3Al and a catalytic amount of $Pd(PPh_3)_4$ afforded the methylated alkenyl sulfide **5** in 80% yield. Hydrolysis with $TiCl_4$ gave the ketone **6**, which completed its 1,2-carbonyl transposition under methylation. The enol phosphate **10** was converted into benzyl methyl ketone in nearly 60% overall yield upon treatment with Et_3Al-$Pd(PPh_3)_4$ reagent and hydrolysis of the simple reduction product **11** isolated in 64% yield (Scheme 6). The ethylated sulfide, PhC(Et)=C(SMe)Me, was isolated in less than 4% yield.

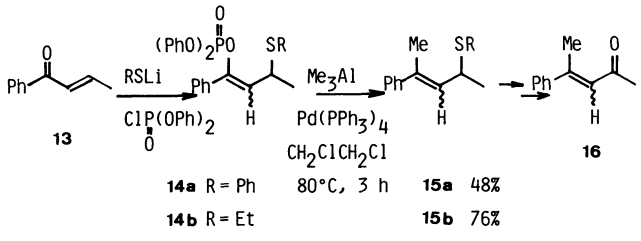


(a) $LiNPr^i_2$, PhSSPh (b) NaH, $ClP(O)(OPh)_2$ (c) Me_3Al, $Pd(PPh_3)_4$, CH_2ClCH_2Cl, 80 °C (d) $TiCl_4$-H_2O, CH_2Cl_2 (e) $TiCl_4$-H_2O, CH_3COOH

Scheme 5.



Scheme 6.



Scheme 7.

Alkylative 1,3-transposition[16] of a carbonyl group could be also achieved (Scheme 7). Enol phosphates **14a, b** prepared by 1,4-addition of RSLi (R=Ph, Et) to an enone **13** and successive phosphorylation were submitted to alkylation with the Me_3Al-$Pd(PPh_3)_4$ system. The alkylated product **15a** was transformed into an enone **16** by the procedures previously reported.[16a]

Experimental

The IR spectra were determined on Shimadzu IR-27-G spectrometer, the mass spectra, on a Hitachi M-80 machine, and the NMR spectra, on a Varian EM-360 spectrometer. The chemical shifts are given in δ, with TMS as the internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. 1,2-dichloroethane was dried on P_2O_5 and distilled. All the experiments were carried out under an argon atmosphere. Purification of product were performed by preparative thin layer chromatography (TLC) or column chromatography on silica gel (Merck Kieselgel 60). Analytical GLPC was performed with a Yanagimoto GCG-550-F or Shimadzu GC-4CPT. Preparative GLPC was performed with a JEOL-JGC-20K apparatus.

Preparation of Enol Diphenyl Phosphates. A solution of a ketone (5.0 mmol) in THF (30 ml) was treated with lithium diisopropylamide (5.5 mmol) at −78 °C for 30 min. To this was added at −78 °C a THF solution of diphenyl phosphorochloridate (1.3 g, 5.5 mmol) and the solution was allowed to warm to 0 °C. After being stirred for 20 min, the mixture was diluted with ether (20 ml), poured into ice-cold water (50 ml), and extracted with ether. The separated organic layer was washed with brine (2×20 ml), dried (Na_2SO_4), and concentrated. The crude product was purified by silica-gel column chromatography(hexane-ethyl acetate).

1-Decylethenyl Diphenyl Phosphate: Bp 168 °C (bath temp, 0.15 Torr, 1 Torr=133.322 Pa); IR (neat): 2950, 2870, 1665, 1600, 1498, 1300, 1190, 1025, 960, 755, 690 cm^{-1}; NMR (CCl_4): δ 0.75—1.00 (bt, *J*=6 Hz, 3H), 1.15—1.50 (m, 16H), 2.17 (t, *J*=7 Hz, 2H), 4.50—4.60 (bm, 1H), 4.88 (t, *J*= 5 Hz, 1H), 7.10—7.40 (m, 10H); MS *m/e* (%): 416 (M^+, 4), 252 (20), 251 (100), 250 (16), 166 (17), 116 (16), 94 (30), 77 (24); Found: C, 69.38; H, 8.13%. Calcd for $C_{24}H_{33}O_4P$: C, 69.21; H, 7.99%.

1-Phenylethenyl Diphenyl Phosphate (1): Bp 174 °C (bath temp, 0.1 Torr); IR (neat): 3080, 1642, 1595, 1495, 1465, 1300, 1188, 1010, 960, 770, 690 cm^{-1}; NMR (CCl_4): δ 5.25—5.38 (m, 2H), 7.05—7.65 (m, 15H); MS *m/e* (%): 353 (M^++1, 5), 352 (M^+, 23), 261 (18), 249 (17), 178 (57), 105 (100), 103 (76), 94 (77), 77 (88); Found: C, 67.89; H, 4.86%. Calcd for $C_{20}H_{17}O_4P$: C, 68,18; H, 4.86%.

4-t-Butyl-1-cyclohexenyl Diphenyl Phosphate (2): Bp 168 °C (bath temp, 0.15 Torr); IR (neat): 2980, 1695, 1595, 1495, 1295, 1190, 1115, 950, 770, 752, 688 cm^{-1}; NMR (CCl_4): δ 0.90 (s, 9H), 1.10—2.35 (m, 7H), 5.35—5.54 (bs, 1H), 7.10—7.45 (m, 10H); MS *m/e* (%): 387 (M^++1, 11), 386 (M^+, 47), 329 (12), 251 (100), 94 (24), 77 (44); Found: C, 68.37; H, 7.10%. Calcd for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04%.

General Procedure for the Reaction between Enol Diphenyl Phosphates and Organoaluminium Compounds in the Presence of $Pd(PPh_3)_4$. Palladium tetrakis(triphenylphosphine) was prepared according to the literature.[17] To a solution of an enol diphenyl phosphate (2.0 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) in 1,2-dichloroethane (10 ml) was added at 25 °C a hexane solution of an organoaluminium compound (4.0 mmol) under an argon atmosphere. The yellow color of the solution turned red immediately in the case of trialkylaluminium. After being stirred for an appropriate time as listed in Table 1, the resulting mixture was diluted with ether (20 ml), poured into 1 M† hydrochloric acid (20 ml), and extracted with

† 1 M=1 mol dm^{-3}

ether. The separated organic layer was washed with brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography or preparative TLC on silica gel using hexane as an eluent.

2-Methyl-1-dodecene: Bp 82 °C (bath temp, 5 Torr); IR (neat): 2930, 2850, 1654, 1470, 1460, 1374, 882 cm^{-1}; NMR (CCl_4): δ 0.89 (bt, J=7 Hz, 3H), 1.10—1.45 (m, 16H), 1.69 (s, 3H), 1.96 (t, J=7 Hz, 2H), 4.61 (s, 2H); MS *m/e* (%): 183 (M^++1, 2), 182 (M^+, 10), 126 (5), 97 (11), 83 (14), 69 (41), 56 (100), 41 (61); Found: C, 85.39; H, 14.37%. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37%.

2-Ethyl-1-dodecene: Bp 86 °C (bath temp, 4 Torr); IR (neat): 2925, 2860, 1648, 1468, 1375, 960, 884 cm^{-1}; NMR (CCl_4): δ 0.87 (m, 3H), 1.00 (t, J=7 Hz, 3H), 1.15—1.45 (m, 16H), 1.70—2.15 (m, 4H), 4.62 (s, 2H); MS *m/e* (%): 196 (M^+, 4), 168 (5), 167 (5), 111 (9), 97 (15), 83 (25), 70 (100), 55 (70); Found: C, 85.55; H, 14.55%. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37%.

2-Decyl-4-phenyl-1-buten-3-yne: Bp 176 °C (bath temp, 2 Torr); IR (neat): 2920, 2850, 1610, 1490, 1468, 1442, 890, 750, 686 cm^{-1}; NMR (CCl_4): δ 0.88 (bt, J=6 Hz, 3H), 1.15 1.80 (m, 16H), 2.22 (bt, J=6 Hz, 2H), 5.23 (s, 1H), 5.35 (s, 1H), 7.20—7.53 (m, 5H); MS *m/e* (%): 268 (M^+, 4), 210 (4), 168 (9), 154 (14), 142 (15), 141 (100), 140 (29); Found: C, 89.61; H, 10.74%. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51%.

2-Decyl-1-octen-3-yne: Bp 128 °C (bath temp, 2 Torr); IR (neat): 2940, 2860, 1614, 1468, 1375, 885 cm^{-1}; NMR (CCl_4): δ 0.75—1.05 (m, 6H), 1.15—1.75 (m, 20H), 2.05 (t, J=7 Hz, 2H), 2.24 (t, J=6 Hz, 2H), 5.04 (s, 1H), 5.08 (s, 1H); MS *m/e* (%): 248 (M^+, 2), 191 (11), 149 (11), 135 (11), 122 (63), 108 (33), 107 (100), 93 (88), 79 (52); Found: C, 87.17; H, 13.20%. Calcd for $C_{18}H_{32}$: C, 87.02; H, 12.98%.

(E)-*2-Decyl-1,3-nonadiene*: Bp 175 °C (bath temp, 2 Torr); IR (neat): 2970, 2925, 2855, 1608, 1468, 1460, 962, 880 cm^{-1}; NMR (CCl_4): δ 0.73—1.07 (m, 6H), 1.07—1.73 (m, 22H), 1.73—2.27 (m, 4H), 4.77 (s, 2H), 5.57 (dt, J=15, 6 Hz, 1H), 5.97 (d, J=15 Hz, 1H); MS *m/e* (%): 264 (M^+, 8), 193 (14), 138 (82), 95 (91), 82 (72), 81 (100), 55 (58); Found: C, 86.57; H, 13.74%. Calcd for $C_{19}H_{36}$: C, 86.28; H, 13.72%.

2-Phenyl-1-butene: Bp 104 °C (bath temp, 15 Torr); IR (neat): 3090, 2960, 2930, 1630, 1498, 1465, 1445, 890, 770, 698 cm^{-1}; NMR (CCl_4): δ 1.01 (t, J=7.5 Hz, 3H), 2.47 (q, J= 7.5 Hz, 2H), 4.98 (s 1H), 5.18 (s, 1H), 7.00—7.40 (m, 5H); MS *m/e* (%): 132 (M^+, 66), 117 (100), 115 (28), 103 (53), 91 (33), 78 (36), 77 (46), 51 (62). The compound was identical with the authentic sample.[18]

2,4-Diphenyl-1-buten-3-yne: This compound (clear liquid) polymerized easily at 0 °C to give a pale yellow viscous liquid. IR (neat): 3070, 1604, 1576, 1494, 1448, 1335, 892, 753, 688 cm^{-1}; NMR (CCl_4): δ 5.64 (s, 1H), 5.86 (s, 1H), 7.15—7.75 (m, 10H); MS *m/e* (%): 205 (M^++1, 31), 204 (M^+, 100), 203 (54), 202 (54), 126 (23), 77 (39); Found: *m/e* 204.0895. Calcd for $C_{16}H_{12}$: M, 204.0940.

4-t-Butyl-1-methyl-1-cyclohexene: Bp 60 °C (bath temp, 9 Torr); IR (neat): 2975, 1675, 1390, 1360, 1242, 1175, 800 cm^{-1}; NMR (CCl_4): δ 0.86 (s, 9H), 1.00—1.43 (m, 3H), 1.60 (s, 3H), 1.67—1.98 (m, 4H), 5.29 (bs, 1H); MS *m/e* (%): 152 (M^+, 14), 137 (7), 123 (5), 109 (17), 95 (59), 81 (40), 57 (100); Found: C, 86.95; H, 13.00%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%.

4-t-Butyl-1-(phenylethynyl)-1-cyclohexene: Bp 152 °C (bath temp, 2 Torr); IR (neat): 2950, 1598, 1492, 1364, 750, 688 cm^{-1}; NMR (CCl_4): δ 0.89 (s, 9H), 1.04—1.50 (m, 3H), 1.65—2.37 (m, 4H), 6.06 (bs, 1H), 7.12—7.50 (m, 5H); MS *m/e* (%): 238 (M^+, 23), 181 (18), 167 (27), 166 (21), 154 (66), 153 (26), 57 (100); Found: C, 90.89; H, 9.51%. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30%.

(E)- *and* (Z)-*1-Phenyl-1-prophenyl Diethyl Phosphate*.[9] A mixture of α-bromopropiophenone (4.26 g, 20 mmol) and triethyl phosphite (4.15 g, 25 mmol) was heated at 100 °C for 24 h and washed with water (2×50 ml) to give a crude mixture containing two isomeric enol phosphates and *O,O'*-diethyl 1-benzoylethyl phosphonate in a ratio of *ca.* 3:1:1. The product was carefully separated by column chromatography (benzene–diethyl ether, 20:1) on silica gel (500 g). (*E*)-Isomer: Minor product (8% isolated yield); bp 96 °C (bath temp, 0.1 Torr); IR (neat): 3000, 1670, 1450, 1368, 1270, 1200, 1020, 884, 765, 698 cm^{-1}; NMR (CCl_4): δ 1.27 (t, J= 6 Hz, 6H), 1.75 (dd, J_{H-H}=7 Hz, J_{P-H}=3 Hz, 3H), 4.00 (dt, J_{H-H}=6 Hz, J_{P-H}=6 Hz, 4H), 5.68 (dq, J_{P-H}=2 Hz, J_{H-H}=7 Hz, 1H), 7.15—7.53 (m, 5H); MS *m/e* (%): 270 (M^+, 34), 155 (100), 127 (45), 116 (50), 115 (34), 99 (46). (*Z*)-Isomer: Major product (48% isolated yield); bp 94 °C (bath temp, 0.1 Torr); IR (neat): 2980, 1668, 1495, 1446, 1390, 1268, 1160, 1020, 882, 760, 690 cm^{-1}; NMR (CCl_4): δ 1.23 (t, J=6 Hz, 6H), 1.85 (dd, J_{H-H}=7 Hz, J_{P-H}=3 Hz, 3H), 4.00 (dt, J_{P-H}=6 Hz, J_{H-H}=6 Hz, 4H), 5.57 (dq, J_{P-H}=1.5 Hz, J_{H-H}=7 Hz, 1H), 7.05—7.55 (m, 5H); MS *m/e*(%): 270 (M^+, 32), 155 (100), 127 (45), 116 (55), 115 (34), 99 (50).

(E)-*2-Phenyl-2-butene*:[19] A hexane solution of trimethylaluminium (1.0 M, 40 ml, 4.0 mmol) was added at 25 °C to a stirred solution of (Z)-1-phenyl-1-propenyl diethyl phosphate (0.54 g, 2.0 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) in 1,2-dichloroethane (15 ml). The resulting mixture was heated at 80 °C for 3 h. After a usual workup, the crude product was purified by silica-gel column chromatography using hexane as an eluent to give (*E*)-2-phenyl-2-butene in 88% yield (0.23 g) as a colorless liquid: Bp 98 °C (bath temp, 20 Torr); IR (neat): 3040, 2930, 1650, 1600, 1500, 1448, 1382, 1022, 826, 750, 694 cm^{-1}; NMR (CCl_4): δ 1.79 (d, J=7 Hz, 3H), 2.02 (s, 3H), 5.76 (q, J=7 Hz, 1H), 7.03—7.37 (m, 5H); MS *m/e* (%): 132 (M^+, 86), 117 (100), 115 (20), 91 (18).

The isomeric purity of the crude product was determined by GLPC analysis (10% PEG 20 M, 2 m, 100 °C). (*E*)-Isomer: T_r=8.5 min. (*Z*)-Isomer: T_r=4.1 min.

(Z)-*2-Phenyl-2-butene*:[19] Treatment of (*E*)-1-phenyl-1-propenyl diethyl phosphate (0.54 g, 2.0 mmol) dissolved in 1,2-dichloroethane (15 ml) with trimethylaluminium (1.0 M of a hexane solution, 4.0 ml, 4.0 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) at 80 °C for 3 h gave the title (*Z*)-olefin in 84% yield (0.22 g). Bp 100 °C (bath temp, 20 Torr); IR (neat): 3040, 2930, 1650, 1602, 1500, 1450, 1380, 1260, 1024, 785, 750 cm^{-1}; NMR (CCl_4): δ 1.53 (d, J=7 Hz, 3H), 2.00 (s, 3H), 5.49 (q, J=7 Hz, 1H), 6.95—7.40 (m, 5H); MS *m/e* (%): 132 (M^+, 100), 117 (77), 91 (22).

3-Butyl-1-cyclohexenyl Diphenyl Phosphate. Butyllithium (2.5 ml of a 1.6 M hexane solution, 4.0 mmol) was added to a suspension of copper(I) iodide (0.19 g, 2.0 mmol) in ether (20 ml) at −23 °C under an argon atmosphere. After stirring at −23 °C for 20 min, the reaction mixture was cooled to −78 °C. A solution of 2-cyclohexen-1-one (0.19 g, 2.0 mmol) in ether (3.0 ml) was added and the resulting mixture was kept there for 1 h. A solution of diphenyl phosphorochloridate (0.59 g, 2.2 mmol) in ether (3.0 ml) was added and the mixture was stirred at −78 °C for 1 h, then warmed to 25 °C. Water (5.0 ml) was added and the mixture was filtered through a pad of Celite 545. The filtrate was washed with water (2×10 ml), dried over anhydrous sodium sulfate, and concentrated to give a pale yellow oil. Purification by column chromatography on silica gel (50 g) with hexane–ethyl acetate (10:1) as an eluent afforded a milky oil (0.61 g, 78%): Bp 162 °C (bath temp, 0.15 Torr); IR (neat): 2950, 1682, 1595, 1495, 1296, 1190, 950, 770, 750, 688 cm^{-1}; NMR (CCl_4): δ 0.87 (bt, J=6

Hz, 3H), 1.03—1.42 (m, 6H), 1.50—1.90 (m, 4H), 1.97—2.30 (m, 3H), 5.37 (bs, 1H), 7.04—7.42 (m, 10H); MS *m/e* (%): 386 (M^+, 27), 330 (20), 329 (100), 251 (71), 136 (23), 94 (17), 79 (32), 77 (61); Found: C, 68.50; H, 7.12%. Calcd for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04%.

3-Butyl-1-methyl-1-cyclohexene: Bp 127 °C (bath temp, 1 atm); IR (neat): 2950, 2860, 1460, 1380, 810 cm^{-1}; NMR (CCl_4): δ 0.91 (t, J=5 Hz, 3H), 1.05—1.46 (bm, 6H), 1.50—2.04 (m, 10H), 5.21 (bs 1H); MS *m/e* (%): 152 (M^+, 54), 96, (53), 95 (100), 81 (43), 79 (33), 67 (77), 55 (47); Found: C, 86.81; H, 13.30%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%.

1-Phenylthio-1-pentenyl Diphenyl Phosphate (3). *S*-Phenyl pentanethioate was prepared by the reaction of the acid chloride with an excess of benezenethiol in pyridine. *S*-Phenyl pentanethioate (0.97 g, 5.0 mmol) dissolved in THF (25 ml) was treated with lithium diisopropylamide (5.5 mmol) at −78 °C. The resulting lithium enolate was trapped by diphenyl phosphorochloridate (1.48 g, 5.5 mmol) at 0 °C. The mixture was diluted with ether (20 ml) and poured into ice-cold water. The separated organic layer was washed with brine (2×20 ml), dried (Na_2SO_4), and concentrated. Purification of the crude product by silica-gel column chromatography (hexane–ethyl acetate, 10:1) gave the desired phosphate **3** in 89% yield (1.89 g). This compound decomposes at 140 °C (0.05 Torr). IR (neat): 3080, 2975, 1640, 1596, 1499, 1302, 1192, 960 cm^{-1}; NMR (CCl_4): δ 0.92 (t, J=7 Hz, 3H), 1.10—1.67 (m, 2H), 1.90—2.44 (m, 2H), 5.89 (dt, J=3, 7 Hz, 1H), 6.90—7.35 (m, 15H); MS *m/e* (%): 426 (M^+, 12), 251 (89), 177 (96), 176 (100), 147 (90), 143 (74), 110 (90), 99 (79), 77 (87); Found: C, 64.74; H, 5.46%. Calcd for $C_{23}H_{23}O_4PS$: C, 64.78; H, 5.44%.

2-Phenyl-1-(phenylthio)ethenyl Diphenyl Phosphate: This compound was prepared by treating *S*-phenyl 2-phenylethanethioate first with lithium diisopropylamide and then with diphenyl phosphorochloridate in THF. This phosphate decomposes at 150 °C (0.05 Torr). IR (neat): 3080, 1620, 1595, 1498, 1280, 1188, 945 cm^{-1}; NMR (CCl_4): δ 6.80—7.60 (m, 20H), 6.86 (d, J=2 Hz, 1H); MS *m/e* (%): 460 (M^+, 0.2), 342 (73), 306 (51), 250 (71), 109 (80), 94 (77), 86 (100), 77 (88), 65 (92); Found: *m/e* 460.0861. Calcd for $C_{26}H_{21}O_4PS$: M, 460.0899.

Cross-coupling Reactions between Organoaluminium Reagents and Enol Phosphates Derived from Thiocarboxylic S-Esters. A hexane solution of trimethylaluminium (1.0 M, 4.0 ml, 4.0 mmol) was added at 25 °C to a benzene (15 ml) solution of enol phosphate (2.0 mmol) derived from thiocarboxylic *S*-ester containing a catalytic amount of $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) under an argon atmosphere. After being stirred at 25 °C for an appropriate time, as listed in Table 2, the mixture was diluted with ether (20 ml) and poured into 1 M hydrochloric acid (20 ml). The separated organic layer was washed with brine (2×20 ml), dried over sodium sulfate, and concentrated. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate).

(E)- *and* (Z)-*1-Methyl-1-pentenyl Phenyl Sulfide.* TLC (hexane) showed two UV active bands, R_f=0.50 (23%, isolated yield) and R_f=0.40 (60%, isolated yield). Faster moving band: Bp 75 °C (bath temp, 0.08 Torr); IR (neat): 2970, 1634, 1588, 1484, 1442, 1380, 1056, 1025, 736, 686 cm^{-1}; NMR (CCl_4): δ 0.95 (t, J=7 Hz, 3H), 1.42 (tq, J=7, 7 Hz 2H), 1.87 (s, 3H), 2.27 (dt, J=7, 7 Hz, 2H), 5.71 (bt, J=7 Hz, 1H); MS *m/e* (%): 192 (M^+, 96), 163 (100), 136 (52), 130 (42), 110 (24); Found: C, 75.19; H, 8.43%. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39%. Slower moving band: Bp 72 °C (bath temp, 0.08 Torr); IR (neat): 2970, 1636, 1588, 1482, 1442, 1380, 1150, 1070, 1026, 896, 736, 686 cm^{-1}; NMR (CCl_4): δ 0.94 (t, J=7 Hz, 3H), 1.43 (tq, J=7, 7 Hz, 2H). 1.84 (s, 3H), 2.24 (dt, J=7, 7 Hz, 1H), 5.74 (bt, J=7 Hz, 1H), 6.94—7.30 (m, 5H); MS *m/e* (%): 192 (M^+, 99), 163 (100), 136 (57), 130 (41), 110 (26); Found: C, 74.89; H, 8.44%. Calcd for $C_{12}H_{16}S$: C, 74,94; H, 8.39%.

1-Pentenyl Phenyl Sulfide. GLPC analysis Silicone OV-17, 2 m, 140 °C) of the product generated by the reaction of enol phosphate **3** and triethylaluminium indicated two peaks, T_r=5.5 min (1-pentenyl phenyl sulfide) and T_r=7.3 min (1-ethyl-1-pentenyl phenyl sulfide). The analytically pure samples of both compounds were prepared by preparative GLPC (3% Silicone OV-17, 2 m). Bp 100 °C (bath temp, 1 Torr); IR (neat): 2970, 1612, 1590, 1488, 1444, 1092, 1026, 952, 734, 684 cm^{-1}; NMR (CCl_4): δ 0.94 (bt, 3H), 1.18—1.72 (m, 2H), 1.93—2.35 (m, 2H), 5.55—6.22 (m, 2H), 6.98—7.33 (m, 5H); MS *m/e* (%): 178 (M^+, 87), 149 (100), 110 (27); Found: C, 74.16; H, 8.01%. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91%.

1-Ethyl-1-pentenyl Phenyl Sulfide: Bp 75 °C (bath temp, 0.08 Torr); IR (neat): 2970, 1634, 1588, 1484, 1442, 1380, 1068, 1025, 895, 736, 686 cm^{-1}; NMR (CCl_4): δ 0.93 (t, J=7 Hz, 3H), 1.03 (t, J=7 Hz, 3H), 1.17—1.64 (m, 2H), 1.97—2.44 (m, 2H), 5.79 (bt, J=7 Hz, 1H), 6.85—7.27 (m, 5H); MS *m/e* (%): 206 (M^+, 100), 177 (68), 135 (85), 110 (33), 67 (43), 55 (84); Found: C, 75.83; H, 8.94%. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79%.

1-(Phenylethynyl)-1-pentenyl Phenyl Sulfide: Bp 106 °C (bath temp, 0.04 Torr); IR (neat): 3070, 2970, 2210, 1588, 1495, 1485, 1445, 1280, 1070, 1024 cm^{-1}; NMR (CCl_4): δ 1.03 (t, J=7.5 Hz, 3H), 1.28—1.76 (m, 2H), 2.39 (dt, J=7, 7 Hz, 2H), 6.23 (t, J=7 Hz, 1H), 6.85—7.50 (m, 10H); MS *m/e* (%): 278 (M^+, 100), 249 (77), 235 (15), 216 (18), 154 (35), 141 (33), 115 (34), 91 (35); Found: *m/e* 278.1139. Calcd for $C_{19}H_{18}S$: M, 278,1128.

(E)-*1-Butylidene-2-heptenyl Phenyl Sulfide*: Bp 104 °C (bath temp, 0.07 Torr); IR (neat): 2920, 2850, 1645, 1586, 1480, 1440, 1026, 960, 899 cm^{-1}; NMR (CCl_4): δ 0.73—1.68 (m, 14H), 1.87—2.15 (m, 2H), 2.36 (dt, J=7, 7 Hz, 2H), 5.93—6.27 (m, 3H), 7.05—7.35 (m, 5H); MS *m/e* (%): 274 (M^+, 79), 259 (32), 245 (50), 231 (21), 203 (54), 197 (23), 109 (59). 79 (100); Found: *m/e* 274.1775. Calcd for $C_{18}H_{28}S$: M, 274.1709.

1-Phenyl-2-phenylthio-1-propene: Bp 115 °C (bath temp, 0.09 Torr); IR (neat): 3070, 1600, 1584, 1478, 1442, 1023, 904, 845, 745, 690 cm^{-1}; NMR (CCl_4): δ 2.00, 2.07 (s, 3H, (*E*) and (*E*)-isomeric mixture), 6.58 (bs, 1H), 7.03—7.53 (m, 10H); MS *m/e* (%): 226 (M^+, 84), 211 (25), 115 (100), 91 (53); Found: C, 79.75; H, 6.29%. Calcd for $C_{15}H_{14}S$: 79.60; H, 6.23%.

1-Phenyl-2-(phenylthio)ethene and 1-Phenyl-2-phenylthio-1-butene. These compounds could not be separated well by GLPC (PEG 20M, PEG 6000, Silicone OV-17, or SE-30). The ratio of ethylated and hydrogenated products was determined by NMR analysis. Spectral data of the mixture are as follows. NMR (CCl_4): δ 1.13 (t, J=7 Hz, C=C(SPh)$CH_2C\underline{H}_3$), 2.27 (q, J=7 Hz, C=C(SPh)$C\underline{H}_2CH_3$), 6.3, 6.45 (d, J=11 Hz, $C{=}C\begin{smallmatrix}\underline{H}\\ \diagup\\ \underline{H}\diagdown\end{smallmatrix}$), 6.68 (s, $PhC\underline{H}$=C(SPh)-Et), 6.61, 6.74 (d, J=15 Hz, $C{=}C\begin{smallmatrix}\underline{H}\diagdown\\ \\ \underline{H}\diagup\end{smallmatrix}$), 7.03—7.54 (m, 10H); MS *m/e* (%): 240 (M^+ of ethylated compound, 64), 212 (M^+ of hydrogenated product 100). Hydrogenated product, 1-phenyl-2-(phenylthio)ethene ((*E*)- and (*Z*)-isomeric mixture), was prepared independently according to the literature.[20] NMR (CCl_4): δ 6.35 and 6.45 (d, J=11 Hz, 2H of (*Z*)-isomr), 6.61 and 6.74 (d, J=15 Hz, 2H of (*E*)-isomer), 6.99—7.53 (m, 10H); MS *m/e* (%): 212 (M^+, 100, 178 (29), 167 (29), 121 (39), 77 (50).

Hydrolysis of Vinyl Sulfide Derivatives with $TiCl_4$-H_2O System.[13] To a stirred dichloromethane (5 ml) solution of vinyl sulfide substrate (1.0 mmol) was added at 25 °C a

dichloromethane solution of titanium tetrachloride (1.0 M, 2.0 ml, 2.0 mmol) and water (72 mg, 4.0 mmol) successively. The mixture was stirred at 25 °C for several hours. Then ether (10 ml) was added to the reaction mixture and the whole was poured into water (10 ml). The separated organic layer was washed with brine (2×10 ml), dried (Na_2SO_4), and concentrated. Purification was carried out by preparative TLC (hexane–ether).

2-Hexanone and benzyl methyl ketone were identical with the authentic samples.

(E)-6-Dodecen-5-one: Mercury(II) chloride (0.54 g, 2.0 mmol) was added to a solution of (*E*)-1-butylidene-2-heptenyl phenyl sulfide (0.14 g, 0.5 mmol) in CH_3CN-H_2O (3:1, 8 ml) at 25 °C. The resulting mixture was heated at 100 °C for 8 h with rapid stirring. The cold mixture was filtered and the residue was washed with ethyl acetate (2×10 ml). The separated organic layer was washed with water (10 ml) and brine (2×10 ml), dried over magnesium sulfate, and concentrated. Purification by preparative TLC (hexane–ethyl acetate, 10:1) afforded the enone in 65% yield (59 mg). Bp 89 °C (bath temp, 1.5 Torr); IR (neat): 2975, 2950, 1700, 1680, 1635, 1472, 982, 726 cm^{-1}; NMR (CCl_4): δ 0.93 (bt, J=7 Hz, 6H), 1.07—1.80 (m, 10H), 2.00—2.51 (m, 4H) 5.92 (d, J=16 Hz, 1H), 6.65 (dt, J=16, 7 Hz, 1H); MS *m/e* (%): 182 (M^+, 1), 153 (1), 140 (15), 125 (40), 111 (17), 55 (100); Found: C, 78.95; H, 12.39%. Calcd for $C_{12}H_{22}O$: C, 79.06; 12.16%.

4-t-Butyl-2-phenylthio-1-cyclohexenyl Diphenyl Phosphate (4). Treatment of 4-*t*-butyl-2-phenylthiocyclohexanone (0.79 g, 3.0 mmol) with sodium hydride (60%, 0.13 g, 3.3 mmol) and diphenyl phosphorochloridate (0.89 g, 3.3 mmol) in THF (15 ml) at 0 °C afforded the title phosphate **4** (78% yield from 4-*t*-butylcyclohexanone) as a pale yellow liquid: Bp 175 °C (bath temp, 0.05 Torr); IR (neat): 3080, 2980, 1666, 1595, 1492, 1365, 1290, 1185, 950, 770, 750 cm^{-1}; NMR (CCl_4): δ 0.84 (s, 9H), 1.20—2.00 (m, 2H), 2.00—2.50 (m, 3H), 2.68—3.00 (m, 2H), 7.00—7.50 (m, 15H); MS *m/e* (%): 494 (M^+, 100), 329 (52), 251 (42), 187 (58), 160 (71), 57 (59); Found: C, 68.07; H, 6.31%. Calcd for $C_{28}H_{31}O_4PS$: C, 68.00; H, 6.32%.

1-Phenyl-2-phenylthio-1-propenyl Diphenyl Phosphate (7). Treatment of 2-phenylthiopropiophenone (0.73 g, 3.0 mmol) dissolved in THF with lithium diisopropylamide (3.3 mmol) and diphenyl phosphorochloridate (0.89 g, 3.3 mmol) at °C gave title phosphate **7** (64% yield from propiophenone) as a pale yellow liquid: Bp 176 °C (bath temp, 0.05 Torr); IR (neat): 3070, 1592, 1492, 1442, 1298, 1186, 1060, 955, 686 cm^{-1}; NMR (CCl_4): δ 1.78 and 2.00 (d, J=3 and 2 Hz respectively, 3H, (*E*)- and (*Z*)-isomeric mixture), 6.95—7.60 (m, 20H); MS *m/e* (%): 474 (M^+, 4), 326 (100), 325 (67), 251 (18), 233 (18), 170 (28), 94 (29); Found: C, 68.47; H, 5.15%. Calcd for $C_{27}H_{23}O_4PS$: C, 68.34; H, 4.89%.

5-t-Butyl-2-methyl-1-cyclohexenyl Phenyl Sulfide (5). To a solution of enol diphenyl phosphate **4** (0.99 g, 2.0 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) in 1,2-dichloroethane (10 ml) was added at 25 °C a hexane solution of trimethylaluminium (1.0 M, 5.0 ml, 5.0 mmol). The resulting mixture was heated at 80 °C for 4 h. After the usual workup, as described above, the crude product was purified by silica-gel column chromatography (hexane–ethyl acetate, 10:1) to give the sulfide **5** (0.42 g, 80%) as a colorless liquid: Bp 132 °C (bath temp, 2 Torr); IR (neat): 2960, 1752, 1588, 1482, 1442, 1364, 1220, 1020, 735, 688 cm^{-1}; NMR (CCl_4): δ 0.83(s, 9H), 1.13—1.46 (m, 3H), 1.92 (s, 3H), 1.46—2.35 (m, 4H), 7.00—7.40 (m, 5H); MS *m/e* (%): 260 (M^+, 100), 203 (8), 95 (44), 93 (42), 57 (78); Found: *m/e* 260.1582. Calcd for $C_{17}H_{24}S$: M, 260.1600.

2-Phenyl-3-phenylthio-2-butene (8): Bp 138 °C (bath temp, 2 Torr); IR (neat): 3080, 2940, 1590, 1484, 1445, 1024, 738, 700, 690 cm^{-1} NMR (CCl_4): δ 1.80, 2.03, 2.16, 2.30 (s, total 6H, (*E*)- and (*Z*)-isomeric mixture), 7.00—7.50 (m, 10H); MS *m/e* (%): 240 (M^+, 60), 132 (23), 131 (100), 91 (76); Found: C, 79.90; H, 6.75%. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71%.

2-Methyl-5-t-butylcyclohexanone (6).[21] Alkenyl sulfide **5** was subjected to hydrolysis with titanium tetrachloride according to the literature.[13] Bp 108 ° (bath temp, 3 Torr); IR (neat): 2970, 1708, 1448, 1364, 1220, 1052 cm^{-1}; NMR (CCl_4): δ 0.95 (s, 9H), 0.82—2.55 (m, 11H); MS *m/e* (%): 168 (M^+, 17), 112 (55), 111 (40), 57 (100), 55 (72).

3-Phenyl-2-butanone (9):[22] Bp 98 °C (bath temp, 5 Torr); IR neat): 3030, 2975, 2935, 1715, 1492. 1358, 1195, 950, 765, 702 cm^{-1}; NMR (CCl_4): δ 1.34 (d, J=7 Hz, 3H), 1.96 (s, 3H), 3.64 (q, J=7 Hz, 1H), 7.00—7.45 (m, 5H); MS *m/e* (%): 148 (M^+, 11), 133 (5), 105 (100), 79 (10), 77 (10), 43 (16).

2-Methylthio-1-phenyl-1-propenyl Diphenyl Phosphate (10). The enol phosphate **10** was prepared by treating α-(methylthio)propiophenone with lithium diisopropylamide and diphenyl phosphorochloridate in THF. TLC analysis (hexane–ethyl acetatea, 2:1) of the crude product showed two UV active bands, R_f=0.61 (49%, isolated yield) and R_f=0.51 (36%, isolated yield). The two isomers were separated by silica-gel column chromatography (hexane–ethyl acetate, 10:1). Faster moving band (**10a**): Bp 160 °C (bath temp, 0.15 Torr); IR (neat): 1590, 1488, 1294, 1184, 1055, 945, 684 cm^{-1}; NMR (CCl_4): δ 2.02 (d, J=2 Hz, 3H), 2.06 (s, 3H), 6.80—7.42 (m, 15H); MS *m/e* (%): 412 (M^+, 12), 306 (56), 251 (83), 250 (89), 170 (37), 147 (25), 94 (100); Found: *m/e* 412.0871. Calcd for $C_{22}H_{21}O_4PS$: M, 412.0899. Slower moving band (**10b**): Bp 160 °C (bath temp, 0.15 Torr); IR (neat): 1600, 1500, 1304, 1200, 1092, 955, 688 cm^{-1}; NMR (CCl_4): δ 1.92 (d, J=3 Hz, 3H), 2.22 (s, 3H), 6.80—7.40 (m, 15H); MS *m/e* (%): 412 (M^+, 50), 251 (19), 162 (46), 147 (100), 115 (26); Found: *m/e* 412.0882. Calcd for $C_{22}H_{21}O_4PS$: M, 412.0899.

(E)- and (Z)-1-Methyl-2-phenylethenyl Methyl Sulfide (11).[23] Treatment of enol phosphate **10a** dissolved in 1,2-dichloroethane with triethylaluminium (2.0 equiv) and a catalytic amount of $Pd(PPh_3)_4$ (0.1 equiv) at 80 °C for 4 h gave the hydrogenated sulfide **11** in 59% yield (*E*/*Z*=68/32). Meanwhile enol phosphate **10b** afforded (*E*)-isomer in 72% yield as the sole product under the same conditions. (*E*)-Isomer: Bp 94 °C (bath temp, 4 Torr); R_f=0.21 (hexane): IR (neat): 2920, 1618, 1500, 1440, 1376, 1002, 764, 692 cm^{-1}; NMR (CCl_4): δ 2.06 (s, 3H), 2.30 (s, 3H), 6.10 (s, 1H), 7.10—7.45 (m, 5H); MS *m/e* (%): 164 (M^+, 100), 149 (69), 134 (42), 115 (29), 91 (21). (*Z*)-Isomer: Bp 96 °C (bath temp, 4 Torr); R_f=0.17 (hexane); IR (neat): 2940, 1600, 1500, 1448, 1118, 746, 688 cm^{-1}; NMR (CCl_4): δ 2.17 (s, 3H), 2.24 (s, 3H), 6.33 (s, 1H), 6.95—7.42 (m, 5H); MS; *m/e* (%): 164 (M^+, 100), 149 (68), 134 (59), 115 (69), 91 (27).

1-Phenyl-3-phenylthio-1-butenyl Diphenyl Phosphate (14a). A solution of 1-phenyl-2-buten-1-one (**13**, 0.73 g, 5.0 mmol) in THF (20 ml) was added at −78 °C to a THF solution of lithium benzenethiolate (5.0 mmol) and the whole was stirred at 0 °C for 15 min. To this mixture was added a THF solution of diphenyl phosphorochloridate (5.0 mmol). After being stirred at 0 °C for 20 min, the mixture was diluted with ether (20 ml) and poured into ice-cold water (30 ml). The separated organic layer was washed with brine (2×20 ml), dried (Na_2SO_4), and concentrated. Purification of the crude product gave the desired phosphate **14a** in 74% yield (1.80 g). Bp 166 °C (bath temp, 0.05 Torr); IR (neat): 3075, 1662, 1595, 1498, 1302, 1188, 950 cm^{-1}; NMR (CCl_4): δ 1.36 (d. J=7 Hz, 3H), 4.30 (dq, J=10, 7 Hz, 1H), 5.44 (dd, J=2, 10 Hz, 1H), 6.84—7.50 (m, 20H); MS *m/e* (%): 488 (M^+, 1), 380 (33), 379 (100), 342 (35), 252 (49), 251 (98), 129 (99), 128 (97), 109 (95), 77 (93), 65 (95); Found: C, 68.60; H, 5.33%. Calcd for $C_{28}H_{25}O_4PS$: C, 68.84; H, 5.16%.

1-Phenyl-3-ethylthio-1-butenyl Diphenyl Phosphate (14b). This compound was prepared by using lithium ethanethiolate instead of lithium benzenethiolate in a manner similar to that described above. Bp 160 °C (bath temp, 0.05 Torr); IR (neat): 3070, 2975, 1660, 1592, 1495, 1186, 950 cm^{-1}; NMR (CCl_4): δ 1.16 (t, J=7 Hz, 3H), 1.27 (d, J=7 Hz,3H), 2.38 (q, J=7 Hz, 2H), 3.95 (dq, J=10, 7 Hz, 1H), 5.46 (dd, J=2, 10 Hz, 1H), 6.83—7.57 (m, 15H); MS m/e (%): 440 (M^+, 6), 379 (15), 251 (100), 190 (47), 175 (37), 129 (66), 77 (58); Found: C, 65.17; H, 5.68%. Calcd for $C_{24}H_{25}O_4PS$: C, 65.44; H, 5.72%.

2-Phenyl-4-phenylthio-2-pentene (15a). Enol diphenyl phosphate **14a** (0.97 g, 2.0 mmol) dissolved in benzene (15 ml) was treated with trimethylaluminium (1.0 M of a hexane solution, 5.0 ml, 5.0 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) at 80 °C for 3 h. After a usual workup,the crude product was purified by preparative TLC (hexane–ethyl acetate, 5:1) to afford the title coupling product **15a** in 48% yield (0.24 g). Bp 117 °C (bath temp, 0.09 Torr); IR (neat): 3080, 2985, 1606, 1592, 1502, 1445, 1200, 1024, 872 cm^{-1}; NMR (CCl_4): δ 1.27, 1.38 (d, J=7 Hz each, 3H, (*E*)- and (*Z*)-isomeric mixture), 1.68, 1.93 (s, 3H), 3.70, 4.00 (dq, J=11, 7 Hz each, 1H), 5.29, 5.53 (bd, J=10 Hz each, 1H), 7.01—7.46 (m, 10H); MS m/e (%): 254 (M^+, 1), 145 (100), 129 (9), 117 (12), 91 (8); Found: m/e 254.1128. Calcd for $C_{17}H_{18}S$: M, 254.1130.

2-Phenyl-4-ethylthio-2-pentene (15b): Bp 95 °C (bath temp, 0.1 Torr); IR (neat): 2980, 2940, 1605, 1503, 1452, 1385, 1272, 1213, 874, 758, 693 cm^{-1}; NMR (CCl_4): δ 1.22 (t, J=7 Hz, 3H), 1.31 (d, J=7 Hz, 3H), 2.05 (s, 3H), 2.41 (q, J=7 Hz, 2H), 3.75 (dq, J=10, 7 Hz, 1H), 5.54 (bd, J=10 Hz, 1H), 7.05—7.43 (m, 5H); MS m/e (%): 206 (M^+, 3), 145 (100), 128 (28), 117 (24), 91 (11); Found: C, 75.69; H, 8.92%. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79%.

(E)-*4-Phenyl-3-penten-2-one (16).* Treatment of allyl sulfide **15a** dissolved in methanol–water with sodium periodate (1.05 equiv) at 0 °C for 4 h afforded the corresponding sulfoxide (**17**, UV active, R_f=0.32 (hexane–ethyl acetate, 1:1)) in 74% yield. The sulfoxide **17** was treated with lithium diisopropylamide (1.5 equiv) and diphenyl disulfide (1.5 equiv) in THF at −78—0 °C for 1 h to give 2-phenyl-4-phenylthio-3-penten-2-ol (**18**, UV active, R_f=0.30 (hexane–ethyl acetate, 5:1). Hydrolysis of the crude sulfide **18** with mercury(II) chloride (1.05 equiv) in acetonitrile–water at 50 °C for 6 h gave the title enone **16** (E/Z=95/5) in 68% yield from **17**. Bp 85 °C (bath temp, 1 Torr); IR (neat): 1730, 1675, 1597, 1490, 1370, 1352, 1240, 1035, 955 cm^{-1}; NMR (CCl_4): δ 2.17 (s, 3H), 2.47 (s, 3H), 6.34 (s, 1H), 7.10—7.52 (m, 5H); MS m/e (%): 160 (M^+, 66), 159 (100), 145 (87), 117 (45), 115 (36), 91 (24). The compound was identical with the authentic sample.[24]

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