Reaction of a Cyclic Phosphonium Ylide with α,β-Unsaturated Thioesters

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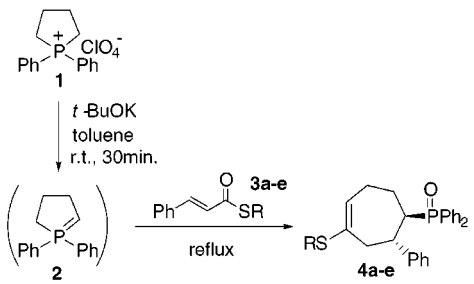
The tandem Michael−intramolecular Wittig reactions of a five-membered cyclic phosphonium ylide (**2**) with α,β-unsaturated thioesters afforded cycloheptene derivatives **4a**−**g** in 29−58% yield. The reaction proceeded via a rigid phosphabicyclic intermediate and supplied the cycloheptene derivatives with high stereoselectivity. On the other hand, although the reaction using *S*-cyclohexyl cyclopentenethiocarboxylate **5a** as a substrate gave a 1:1 mixture of *cis* and *trans* adducts of the corresponding hydroazulene derivatives, the reaction of *S*-*tert*-butyl cyclopentenethiocarboxylate **5b** gave *cis*-adduct as a major product (*cis*:*trans* =17:3).

We reported that the reaction of a five-membered cyclic phosphonium ylide with enones or enoates provided cycloheptene,[1] hydroazulene derivatives,[2] or enol ether[3] of cycloheptanone derivatives with high stereoselectivity via tandem Michael−intramolecular Wittig reactions. In this work, the reaction of the cyclic ylide with α,β-unsaturated thioesters was attempted in order to increase the versatility of this reaction. Thus far, it is clarified that the reaction of a phosphonium ylide with thioesters affords the acyl phosphonium ylide, or in the intramolecular manner, cyclic vinyl sulfides which can be introduced to useful compounds such as β-lactam antibiotics.[4] However, as far as we know the reaction of the ylide with α,β-unsaturated thioester has not been reported.

The reaction of cyclic phosphonium ylide (**2**), generated from the corresponding salt **1** using *t*-BuOK as a base, with *S*-ethyl cinnamthioate **3a** was carried out under several reaction conditions. Although the reaction of the ylide with **3a** in THF both at room temperature (16 h) and at the boiling point (6 h) afforded the corresponding cycloheptenyl sulfide **4a** in only 13% yield, the same reaction when refluxed for a prolonged reaction time (44 h) resulted in an increased yield (31%). Moreover, when this reaction was carried out in refluxing toluene, the desired product was obtained in 47% yield (Table 1). Acyl phosphonium salt or an acyclic product stemmed from the 1,2-addition of the ylide to thioester could not be isolated. The reaction using NaHMDS as a base did not improve the yield of the product.

In addition, the effect of the substituent on sulfur atoms in thioesters was examined for the sake of the enhancement of the yield. The reaction of *S*-cyclohexyl thiocarboxylate **3e** under the similar reaction conditions provided the cycloheptene derivative **4e** in the highest yield (58%). The reaction of *S*-aryl thioate resulted in the lower yield.

Table 1. Reaction of 2 with α,β-Unsaturated thioester 3a−e



entry	R	thioester	time (h)	product	yield (%)[a]
1	Et	**3a**	47	**4a**	47
2	Ph	**3b**	42	**4b**	29
3	*p*-ClC_6H_4	**3c**	39	**4c**	37
4	*i*-Pr	**3d**	40	**4d**	41
5	*c*-C_6H_{11}	**3e**	38	**4e**	58

[a] Isolated yield.

The reaction of the ylide (**2**) with some *S*-cyclohexyl thioates which have a different substituent on the β carbon atom was also attempted. It was clarified that the reaction of thioesters having alkyl groups such as Me or Pr afforded also the corresponding cycloheptenyl sulfides **4f** and **4g** in 54% and 58% yields (Scheme 1).

The structures of **4a**−**g** were confirmed by ^{13}C NMR, ^{13}C DEPT, and ^{1}H NMR spectroscopy and mass spectrometry. Especially, from ^{13}C NMR spectra, the compounds **4a**−**g** were clarified to be a single product because the peaks ascribed to other stereoisomers were not detected (Table 2). The intramolecular Wittig reaction in these reactions was considered to proceed via a similar rigid phosphabicycle to the reaction using enones or enoates because the carbons α, β, and γ to phosphorus had chemical shifts and coupling constants (J_{PC}) very similar to those in cycloheptene derivatives which were obtained from the reaction of **2** with enones or enoates.[1,3]

(1) Fujimoto, T.; Takeuchi, Y.; Kai, K.; Hotei, Y.; Ohta, K.; Yamamoto, I. *J. Chem. Soc., Chem. Commun*. **1992**, 1263−1264.
(2) Fujimoto, T.; Uchiyama, Y.; Kodama, Y.; Ohta, K.; Yamamoto, I.; Kakehi, A. *J. Org. Chem*. **1993**, *58*, 7322−7323.
(3) Fujimoto, T.; Kodama, Y.; Yamamoto, I. *J. Org. Chem*. **1997**, *62*, 6627−6630.
(4) For a review, see: (a) Johnson, A. W. *Ylides and Imines of Phosphorus*; J. Wiley & Sons Inc.: New York, 1993. (b) Murphy, P. J.; Brennan, J. *Chem. Soc. Rev*. **1988**, *17*, 1−30. (c) Becker, K. B. *Tetrahedron* **1980**, *36*, 1717−1745. Recent publications: (d) Hatanaka, M.; Himeda, Y.; Imashiro, R.; Tanaka, Y.; Ueda, I. *J. Org. Chem*. **1994**, *59*, 111−119. (e) Hatanaka, M.; Himeda, Y.; Tanaka, Y.; Ueda, I. *Tetrahedron Lett*. **1995**, *36*, 3211−3214. (f) Greenlee, M. L.; Dininno, F. P.; Sclzmann, T. N. *Heterocycles* **1989**, *28*, 195−202.

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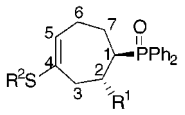
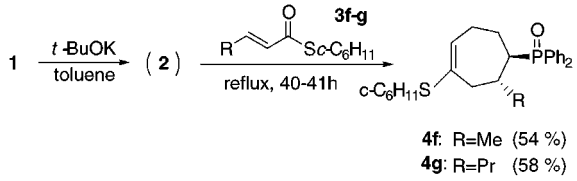
Table 2. ^{13}C Chemical Shifts and $^{13}C-^{31}P$ Coupling Constants in Cycloheptene Derivatives 4a−g[a]



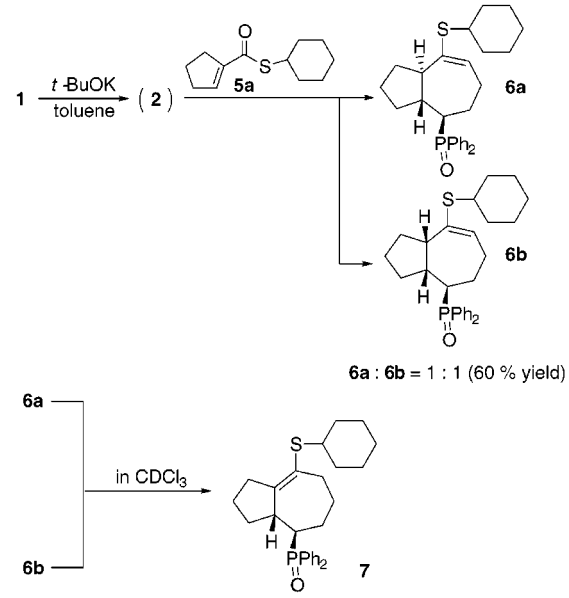
			chemical shifts (ppm) and J_{PC} (Hz)				
compd	R^1	R^2	C_1	C_2	C_3	C_6	C_7
4a	Ph	Et	42.7 (J_{PC} = 69.3)	43.2	39.8 (J_{PC} = 9.3)	30.1 (J_{PC} = 11.7)	24.3 (J_{PC} = 1.5)
4b	Ph	Ph	42.4 (J_{PC} = 69.0)	43.5	39.6 (J_{PC} = 9.2)	29.9 (J_{PC} = 9.8)	24.0 (J_{PC} = 5.5)
4c	Ph	*p*-ClC_6H_4	42.5 (J_{PC} = 68.9)	43.6	39.7 (J_{PC} = 8.3)	30.0 (J_{PC} = 10.3)	24.2 (J_{PC} = 6.8)
4d	Ph	*i*-Pr	42.1 (J_{PC} = 68.9)	42.6	40.0 (J_{PC} = 8.8)	28.8 (J_{PC} = 10.7)	23.7 (J_{PC} = 1.5)
4e	Ph	c-C_6H_{11}	42.8 (J_{PC} = 69.3)	43.7	40.9 (J_{PC} = 8.8)	30.0 (J_{PC} = 11.2)	24.4 (J_{PC} = 1.5)
4f	Me	c-C_6H_{11}	44.1 (J_{PC} = 69.3)	31.1	38.8 (J_{PC} = 3.9)	29.9 (J_{PC} = 13.2)	23.8
4g	Pr	c-C_6H_{11}	42.9 (J_{PC} = 69.3)	35.8	37.7 (J_{PC} = 9.8)	29.8 (J_{PC} = 13.7)	23.6

[a] TMS as an internal standard in $CDCl_3$ was employed.

Scheme 1



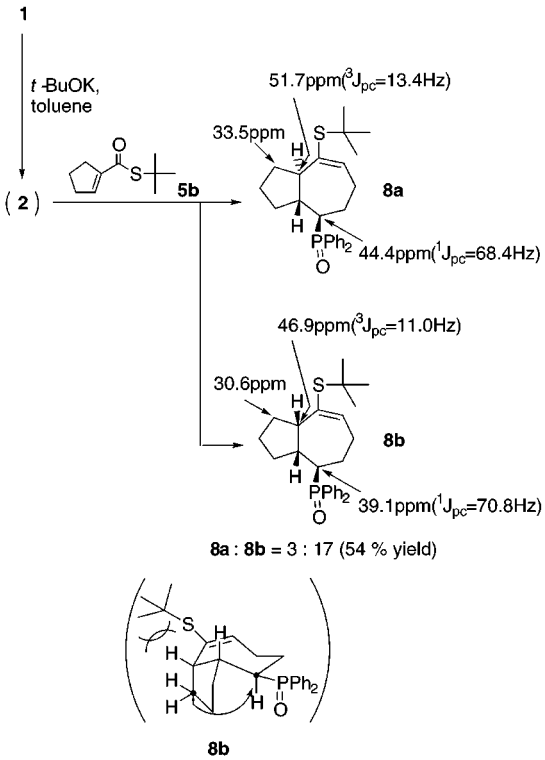
Scheme 2



Accordingly, that *trans* cycloheptenyl sulfides predominantly formed was concluded from these points.

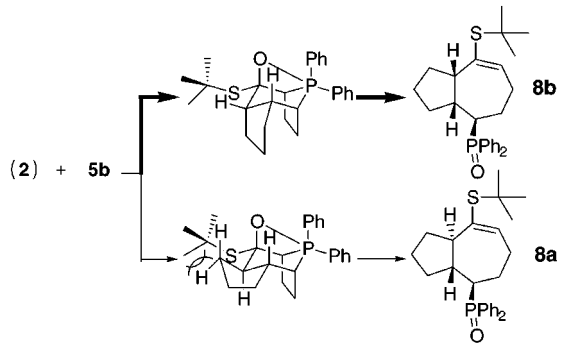
On the other hand, the reaction of the ylide **2** with cyclopentenethiocarboxylate **5a** afforded a 1:1 mixture of two stereoisomers of the corresponding hydroazulene derivatives in 60% yield (Scheme 2). Although these isomers were obviously different compounds on TLC and could be separated by column chromatography, ^{13}C NMR spectra of each showed the same peaks ascribed to **7** in which the double bond of the initial product was thought to be isomerized to the bridgehead position by a trace amount of acid in chloroform-*d*. That is to say, it was clarified that the initial stereoisomers were compounds **6a** and **6b** which have different configuration at the bridgehead position adjacent to vinyl sulfide. The ^{13}C NMR spectra of each compounds in chloroform-*d* containing pyridine displayed the corresponding isomers ascribed to **6a** and **6b**.

Scheme 3

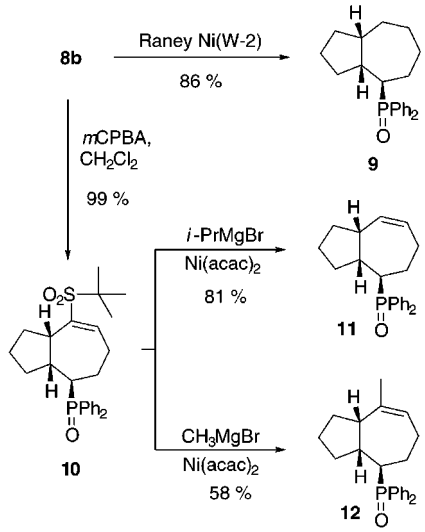


To elucidate if the substituent on the S atom could affect the stereoselectivity, the reaction of the ylide (**2**) with *S-tert*-butyl cyclopentenethiocarboxylate **5b** was attempted. Consequently, a mixture of two hydroazulene derivatives **8a** and **8b** was obtained with a ratio of 3:17 in 54% yield (Scheme 3). Each isomer could be easily separated by column chromatography, and the same isomerization as for **6a**,**b** in $CDCl_3$ was not observed. In the ^{13}C NMR spectra, signals of the carbons α and δ to phosphorus of the major product are shifted upfield by 3−5 ppm compared with the minor product. The upfield shifting of these carbons is considered to be due to the steric compression effect by reason of a γ-gauche relationship between α and δ carbon atoms. Accordingly, it was suggested that the major product would be the *cis*-fused hydroazulene derivative. These results could be supported by the consideration of the transition state in the intramolecular Wittig reaction. The transition state in which the five-membered ring is fused to the six-membered ring in an equatorial−axial manner is thought to be more favorable than the other possible transition

Scheme 4



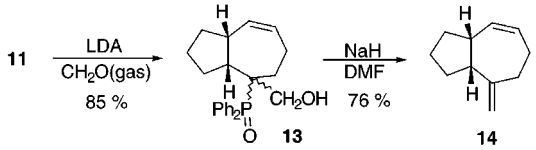
Scheme 5



state (equatorial−equatorial manner) because of the 1,2-diequatorial interaction between the *tert*-butyl group and the methylene group in the five-membered ring (Scheme 4). Consequently, the reaction of *S*-*tert*-butyl thiocarboxylate preferentially afforded the *cis*-fused hydroazulene.

Finally, the sulfur and phosphorus groups in the hydroazulene derivative **8b** were transformed into other functional groups, which are thought to be useful for synthesis of naturally occurring products. Although desulfurization of **8b** using Raney Ni (W-2)[5] gave the saturated hydroazulene derivative **9**, the vinyl sulfone **10** derived from **8b** by oxidation[6] using *m*CPBA could be transformed to the unsaturated hydroazulene **11** by the reaction of *i*-PrMgBr[7] in the presence of $Ni(acac)_2$ (Scheme 5). This reaction sequence (tandem Michael−Wittig reaction followed by desulfurization) is complementary to the reaction of the ylide with α,β-unsaturated aldehydes because the reaction of a cyclic phosphonium ylide with α,β-unsaturated aldehydes does not give cycloheptene derivatives but Wittig product.[1] In addition, the reaction of **10** with MeMgBr[7] in the presence of $Ni(acac)_2$ provided the methyl substituted product **12** in 58% yield. Moreover, the reaction[8] of **11** with formaldehyde in the presence of LDA as a base afforded the alcohol **13** in 85%

Scheme 6



yield, which was converted[9] to **14** by reaction with NaH in 76% yield (Scheme 6).

Experimental Section

Reactions were run in dried glassware under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl. Toluene was distilled from sodium metal. CH_2Cl_2 and DMF were distilled from calcium hydride. Flash column chromatography was carried out on silica gel 60 (Cica-MERCK). 1,1-Diphenylphospholanium perchlorate **1** was prepared by the reaction[10] of tetraphenyldiphosphine with 1,4-dibromobutane followed by exchange of Br^- into ClO_4^- with a saturated aqueous $NaClO_4$ solution. The α,β-unsaturated thioesters were prepared from the reaction of the corresponding acid chlorides with mercaptanes in dry CH_2Cl_2−pyridine (1/1). ^1H and ^{13}C NMR spectra were recorded on a 90 MHz spectrometer using $CDCl_3$ as a solvent. Chemical shifts are reported in δ from TMS as an internal standard. Mass spectra and HRMS were obtained by EI at 70 eV or FAB. Melting points are uncorrected.

General Procedures for the Reaction of Cyclic Phosphonium Ylide 2 with Thioesters 3a−h, 5a, and 5b. A solution of phosphonium salt (0.50 g, 1.47 mmol) and potassium *tert*-butoxide (0.17 g, 1.52 mmol) in dry toluene (10 mL) was stirred at room temperature for 30 min. Then a solution of the thioester (1.50 mmol) in dry toluene (5 mL) was added dropwise to the mixture, and the resulting solution was refluxed for 38−47 h. After being cooled to room temperature, the mixture was quenched with water and extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as eluent.

***trans*-[4-(Ethylthio)-2-phenyl-4-cyclohepten-1-yl]diphenylphosphine Oxide (4a).** The reaction was performed according to the general procedure to give **4a** (0.30 g, 47%) as a white solid: mp 147−150 °C; ^1H NMR δ 1.11 (t, J = 7 Hz, 3H), 2.16−3.08 (m, 10H), 5.54 (brt, 1H), 6.92−7.82 (m, 15H); IR (KBr) 1180 cm^{-1} (P═O), 1700 cm^{-1} (C═C); MS *m*/*z* 432 (M^+); HRMS calcd for $C_{27}H_{29}OPS$ 432.1674, found M^+ 432.1664.

***trans*-[4-(Phenylthio)-2-phenyl-4-cyclohepten-1-yl]-diphenylphosphine Oxide (4b).** The reaction was performed according to the general procedure to give **4b** (0.20 g, 29%) as a white solid.

***trans*-[4-(*p*-Chlorophenylthio)-2-phenyl-4-cyclohepten-1-yl]diphenylphosphine Oxide (4c)**. The reaction was performed according to the general procedure to give **4c** (0.28 g, 37%) as a white solid.

***trans*-[4-(Isopropylthio)-2-phenyl-4-cyclohepten-1-yl]-diphenylphosphine Oxide (4d)**. The reaction of phosphonium salt (0.30 g,0.88 mmol), *t*-BuOK (0.11 g, 0.97 mmol), and thioester (0.18 g, 0.88 mmol) in dry toluene (25 mL) was performed according to the general procedure to give **4d** (0.16 g, 41%) as a white solid.

***trans*-[4-(Cyclohexylthio)-2-phenyl-4-cyclohepten-1-yl]-diphenylphosphine Oxide (4e)**. The reaction of phosphonium salt (0.30 g, 0.88 mmol), *t*-BuOK (0.11 g, 0.97 mmol), and thioester (0.22 g,0.88 mmol) in dry toluene (25 mL) was performed according to the general procedure to give **4e** (0.25 g, 58%) as a white solid.

(5) Bratz, M.; Bullock, W. H.; Overman, L. E.; Takemoto, T. *J. Am. Chem. Soc.* **1995**, *117*, 5958−5966.
(6) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208−1217.
(7) Fabre, J. L.; Julia, M.; Verpeaux, J. N. *Tetrahedron Lett.* **1982**, *23*, 2469−2472.
(8) Warren, S.; Kennard, O.; Cruse, W. B.; Buss, A. D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 243−247.
(9) Cavalla, D.; Warren, S. *Tetrahedron Lett.* **1982**, *23*, 4505−4508.
(10) (a) Muchowski, J. M.; Venuti, M. C. *J. Org. Chem.* **1981**, *46*, 459−461. (b) Yamamoto, I.; Fujimoto, T.; Ohta, K.; Matsuzaki, K. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1537−1539.

***trans*-[4-(Cyclohexylthio)-2-methyl-4-cyclohepten-1-yl]-diphenylphosphine Oxide (4f)**. The reaction of phosphonium salt (0.30 g, 0.88 mmol), *t*-BuOK (0.11 g, 0.97 mmol), and thioester (0.16 g, 0.88 mmol) in dry toluene (25 mL) was performed according to the general procedure to give **4f** (0.20 g, 54%) as a white solid.

***trans*-[4-(Cyclohexylthio)-2-propyl-4-cyclohepten-1-yl]-diphenylphosphine Oxide (4g)**. The reaction of phosphonium salt (0.30 g, 0.88 mmol), *t*-BuOK (0.11 g, 0.97 mmol), and thioester (0.19 g, 0.88 mmol) in dry toluene (25 mL) was performed according to the general procedure to give **4g** (0.23 g, 58%) as a white solid.

2-(Cyclohexylthio)-6-(diphenylphosphinoyl)bicyclo-[5.3.0]-2-decene (6a and 6b). The reaction of phosphonium salt (0.30 g, 0.88 mmol), *t*-BuOK (0.11 g, 0.97 mmol), and thioester (0.19 g, 0.88 mmol) in dry toluene (25 mL) was performed according to the general procedure to give **6a** (0.12 g, 30%) and **6b** (0.12 g, 30%) as white solids. **6a**: mp 153−156 °C; ^{1}H NMR ($CDCl_3$ containing pyridine) δ 0.75−2.91 (m, 24H), 5.77 (brs, 1H), 7.31−7.91 (m, 10H); ^{13}C NMR ($CDCl_3$ containing pyridine) δ 24.34, 26.00 (C × 2), 27.01 ($^2J_{PC}$ = 3.4 Hz), 27.39, 30.72, 33.09, 34.26, 43.32 ($^2J_{PC}$=2.9 Hz), 44.68, 45.28 ($^1J_{PC}$ = 67.8 Hz), 49.82 ($^3J_{PC}$ = 14.7 Hz), and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O); MS *m*/*z* 450 (M^+); HRMS (Fab) calcd for $C_{28}H_{36}OPS$, M + 1, 451.2224, found, M^+ + 1, 451.2212. **6b**: mp 154.5−156.5 °C; ^{1}H NMR ($CDCl_3$ containing pyridine) δ 0.59−3.18 (m, 24H), 5.65 (brs, 1H), 7.14−7.82 (m, 10H); ^{13}C NMR ($CDCl_3$ containing pyridine) δ 24.03, 24.36, 26.03 (C × 2), 27.47 ($^3J_{PC}$ = 15.1 Hz), 28.56, 31.85, 33.00, 38.77 ($^1J_{PC}$ = 71.3 Hz), 43.62 ($^2J_{PC}$ = 2.0 Hz), 44.75, 45.77 ($^3J_{PC}$ = 12.2 Hz), and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O); MS *m*/*z* 450 (M^+); HRMS (Fab) calcd for $C_{28}H_{36}OPS$, M + 1, 451.2224, found, M^+ + 1, 451.2227.

2-(Cyclohexylthio)-6-(diphenylphosphinoyl)bicyclo-[5.3.0]-1-decene (7). **7** was recovered from NMR samples of **6a** and **6b** as a white solid: mp 201−203 °C; ^{1}H NMR δ 0.60−3.26 (m, 25H), 7.30−8.01 (m, 10H); ^{13}C NMR δ 23.50 ($^3J_{PC}$ = 9.2 Hz), 25.33, 26.03 (C × 2), 26.17, 28.37 ($^2J_{PC}$ = 1.8 Hz), 33.86, 34.13, 34.29, 34.64, 36.41 ($^3J_{PC}$ = 3.7 Hz), 40.93 ($^1J_{PC}$ = 68.4 Hz), 42.59 ($^2J_{PC}$ = 1.8 Hz), 44.21, 124.82, 149.41 ($^3J_{PC}$ = 11.0 Hz), and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O), 1700 cm^{-1} (C═C); MS *m*/*z* 450 (M^+); HRMS (Fab) calcd for $C_{28}H_{36}OPS$, M + 1, 451.2224, found, M^+ + 1, 451.2234.

2-(*tert*-Butylthio)-6-(diphenylphosphinoyl)bicyclo[5.3.0]-2-decene (8a and 8b). The reaction of phosphonium salt (0.30 g, 0.88 mmol), *t*-BuOK (0.11 g, 0.97 mmol), and thioester (0.16 g, 0.88 mmol) in dry toluene (25 mL) was performed according to the general procedure to give **8a** (0.03 g, 8%) and **8b** (0.17 g, 46%) as white solids. **8a**: mp 151−154 °C; ^{1}H NMR δ 0.84−2.88 (m, 22H), 6.30 (brs, 1H), 7.28−7.93 (m, 10H); ^{13}C NMR δ 23.38, 27.02 ($^2J_{PC}$ = 1.8 Hz), 27.33 ($^3J_{PC}$ = 6.1 Hz), 31.45, 33.53, 34.81, 42.61 ($^2J_{PC}$ = 2.4 Hz), 44.40 ($^1J_{PC}$ = 68.4 Hz), 45.78, 51.71 ($^3J_{PC}$ = 13.4 Hz), 137.87, 144.32, and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O), 1700 cm^{-1} (C═C); MS *m*/*z* 424 (M^+); HRMS (Fab) calcd for $C_{26}H_{34}OPS$, M + 1, 425.2069, found, M^+ + 1, 425.2076. **8b**: mp 184−185 °C; ^{1}H NMR δ 0.82−3.18 (m, 22H), 6.21 (brs, 1H), 7.30−7.89 (m, 10H); ^{13}C NMR δ 23.24, 24.19, 28.70 ($^3J_{PC}$ = 15.3 Hz), 30.64, 31.29, 31.96 ($^3J_{PC}$ = 2.4 Hz), 39.14 ($^1J_{PC}$ = 70.8 Hz), 43.46 ($^2J_{PC}$ = 1.8 Hz), 46.32, 46.91 ($^3J_{PC}$ = 11.0 Hz), 135.41, 140.23, and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O), 1720 cm^{-1} (C═C); MS *m*/*z* 424 (M^+); HRMS (Fab) calcd for $C_{26}H_{34}OPS$, M + 1, 425.2068, found, M^+ + 1, 425.2068.

6-(Diphenylphosphinoyl)bicyclo[5.3.0]decane (9). A solution of **8b** (0.10 g, 0.24 mmol) in dry ethanol (10 mL) was added dropwise to Raney Ni (1.67 mL, 0.6 g/mL). The mixture was stirred at room temperature overnight. Then Raney Ni was removed by filtration through Celite. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as eluent. **9**: 70 mg (86%); white solid, mp 210−212.5 °C; ^{1}H NMR δ 1.14−2.35 (m, 17H), 7.27−7.92 (m, 10H); ^{13}C NMR δ 22.34, 28.63, 30.47, 31.94 ($^3J_{PC}$ = 14.7 Hz), 32.70 (C × 2), 34.98, 43.17 ($^2J_{PC}$ = 2.0 Hz), 44.56 ($^3J_{PC}$ = 13.2 Hz), 44.51 ($^1J_{PC}$ = 68.4 Hz), and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O), MS *m*/*z* 338 (M^+); HRMS calcd for $C_{22}H_{27}OP$ 338.1799, found M^+ 338.1812.

2-(*tert*-Butylsulfonyl)-6-(diphenylphosphinoyl)bicyclo-[5.3.0]-2-decene (10). To a solution of **8b** (0.30 g, 0.71 mmol) in dry CH_2Cl_2 (10 mL) immersed in an ice bath was added 85% *m*-chloroperoxybenzoic acid (0.35 g, 1.70 mmol) at a rate which caused gentle boiling of the solvent. After the addition, the ice bath was removed and the solution was stirred for an additional hour at room temperature. A 20 mL portion of 10% aqueous sodium sulfite was added, and the mixture was poured into CH_2Cl_2. The organic layer was washed with 30 mL of 10% aqueous sodium carbonate and 30 mL of brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as eluent. **10**: 0.32 g (99%); white solid, mp 250−251 °C; ^{1}H NMR δ 1.25−2.67 (m, 22H), 6.90 (t, *J* = 5.1 Hz, 1H), 7.30−7.92 (m, 10H); ^{13}C NMR δ 22.41, 24.05, 24.70, 28.82 ($^3J_{PC}$ = 10.7 Hz), 34.13, 35.05 ($^3J_{PC}$ = 6.3 Hz), 39.92, 41.74 ($^1J_{PC}$ = 69.3 Hz), 45.90 ($^3J_{PC}$ = 7.8 Hz), 61.28, 140.75, 146.16, and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O), 1700 cm^{-1} (C═C); MS *m*/*z* 456 (M^+); HRMS (Fab) calcd for $C_{26}H_{34}O_3PS$, M + 1, 457.1966, found, M^+ + 1, 457.1953.

6-(Diphenylphosphinoyl)bicyclo[5.3.0]-2-decene (11). A solution of *i*-PrMgBr (3 mL, 0.8 M in dry ether) was added dropwise to a solution of **10** (0.20 g, 0.44 mmol) and $Ni(acac)_2$ (2 mg) in dry ether (7 mL). The resulting solution was stirred at room temperature for 20 h. The mixture was acidified by 10% HCl aqueous solution and then extracted with CH_2Cl_2. The organic layer was washed with aqueous saturated Na_2CO_3 and water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as eluent. **11**: 0.12 g (81%); white solid, mp 187−189 °C; ^{1}H NMR δ 0.94−3.11 (m, 13H), 5.10−5.51 (m, 2H), 7.29−7.96 (m, 10H); ^{13}C NMR δ 22.34, 25.16, 31.53 ($^3J_{PC}$ = 16.6 Hz), 31.83, 32.98, 40.31 ($^3J_{PC}$ = 11.7 Hz), 41.89 ($^1J_{PC}$ = 70.3 Hz), 45.07 ($^2J_{PC}$ = 2.0 Hz), vinylic carbons and aromatic carbons; IR (KBr) 1180 cm^{-1} (P═O), 1700 cm^{-1} (C═C); MS (Fab) *m*/*z* 337 (M^+ + 1); HRMS (Fab) calcd for $C_{22}H_{26}OP$, M + 1, 337.1721, found, M^+ + 1, 337.1721.

6-(Diphenylphosphinoyl)-2-methylbicyclo[5.3.0]-2-decene (12). A solution of MeMgBr (3 mL, 0.8 mol/L in ether) was added dropwise to a solution of **10** (0.20 g, 0.44 mmol) and $Ni(acac)_2$ (2 mg) in dry ether (7 mL) by syringe. The resulting solution was stirred at room temperature for 20 h. The mixture was acidified by addition of a 10% HCl aqueous solution and then extracted with CH_2Cl_2. The organic layer was washed with aqueous saturated Na_2CO_3, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as eluent. **12**: 90 mg (58%); white solid, mp 113−115 °C; ^{1}H NMR δ 0.91−3.04 (m, 16H), 5.35 (brs, 1H), 7.31−7.93 (m, 10H); ^{13}C NMR δ 22.32, 23.97, 24.89, 27.15 ($^3J_{PC}$ = 15.3 Hz), 28.04, 31.79 ($^2J_{PC}$ =1.8 Hz), 39.57 ($^1J_{PC}$ = 70.8 Hz), 45.07 ($^2J_{PC}$ = 2.4 Hz), 44.45 ($^3J_{PC}$ = 12.2 Hz), 122.08, 136.98, and aromatic carbons; IR (KBr) 1160 cm^{-1} (P═O), 1700 cm^{-1} (C═C); MS (Fab) *m*/*z* 351 (M^+ + 1); HRMS (Fab) calcd for $C_{23}H_{28}OP$, M + 1, 351.1878, found, M^+ + 1, 351.1895.

6-(Diphenylphosphinoyl)-6-(hydroxymethyl)bicyclo-[5.3.0]-2-decene (13). A solution of **11** (0.25 g, 0.74 mmol) in dry THF (8 mL) was added dropwise to LDA (5 equiv in dry THF) at 0 °C. The solution was stirred for 30 min at 0 °C, and then after warming to room temperature, the mixture was stirred for 1 h. Gaseous formaldehyde was bubbled until the solution became yellow color. The resulting solution was refluxed for 18 h. After being cooled to room temperature, the mixture was quenched with water and extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using AcOEt−$CHCl_3$ (1/1) as eluent. **13**: 0.23 g (85%); white solid, mp 140−142 °C; IR (KBr) 1160 cm^{-1} (P═O), 1640 cm^{-1} (C═C); MS (Fab) *m*/*z* 367 (M^+ + 1); HRMS (Fab) calcd for $C_{23}H_{28}O_2P$, M + 1, 367.1827, found, M^+ + 1, 367.1836.

6-(Methylene)bicyclo[5.3.0]-2-decene (14). A solution of **13** (0.14 g, 0.38 mmol) in dry DMF (3 mL) was added dropwise to NaH (60% in oil, 0.026 g, 0.65 mmol), and the resulting solution was stirred at 60 °C for 16 h. After being cooled to room temperature, the mixture was quenched with water and extracted with ether. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using *n*-hexane as eluent. **14**: 42.6 mg (76%); colorless liquid; ^{1}H NMR δ 1.16−2.70 (m, 12H), 4.63−4.67 (m, 2H), 5.34−5.38 (m, 2H); ^{13}C NMR δ 23.64, 29.71, 29.95, 34.09, 34.41, 42.32, 49.65, 109.71, 128.11, 134.03, 152.45; IR (KBr) 1640 cm^{-1} (C=C); HRMS (EI) calcd for $C_{11}H_{16}$ 148.1252, found M^+, 148.1247.

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Supporting Information Available: Spectral characterization of **4b**−**g** and ^{13}C NMR spectra of **4e**−**g**, **6a**,**b**, **7**, **8a**,**b**, **9**−**12**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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