Synthesis of β-Keto Phosphonates from Vinyl Phosphates via a 1,3-Phosphorus Migration

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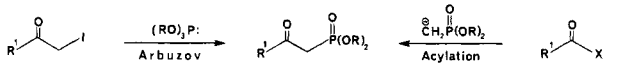
A new method for the preparation of β-keto phosphonates has been developed, involving rearrangement of vinyl phosphates upon treatment with strong base. Because this approach ultimately relies upon electrophilic dialkyl phosphorochloridates as the phosphorus source, it is complementary to such traditional methods for β-keto phosphonate synthesis as the Arbuzov reaction or the acylation of alkyl phosphonate anions. This new method provides ready access to β-keto phosphonates derived from cyclic ketones, compounds that historically have been very inaccessible.

Introduction

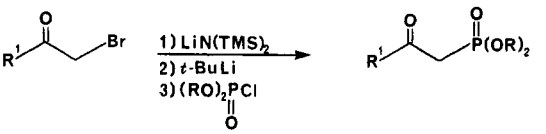
In recent years, β-keto phosphonates have become valuable intermediates in organic synthesis. One important use of these compounds has been the Wadsworth–Horner–Emmons condensation,[2] a very popular method for the synthesis of α,β-unsaturated carbonyl compounds. However, in contrast to the significant number of investigations that have expanded the original scope of the Wadsworth–Horner–Emmons condensation,[3] relatively little work has appeared on new syntheses of β-keto phosphonates. The commonly used methods for preparing β-keto phosphonates are the Arbuzov reaction[4] and the acylation of alkyl phosphonate anions.[5] Both methods suffer from individual restrictions and have a common limitation in their reliance upon nucleophilic phosphorus reagents (Scheme I). As a consequence, with substrates where nucleophilic substitution is difficult (e.g., cyclic systems),[6] or when steric or electronic factors make the phosphorus reagent a poor nucleophile,[7] phosphonate synthesis has been accomplished only on a case-by-case basis.[8]

Our research has focused on potential routes to β-keto phosphonates that rely upon electrophilic phosphorus reagents, and we have developed one such route from α-bromo ketones to β-keto phosphonates (Scheme II).[9] More recently we have discovered a 1,3-phosphorus migration that provides β-keto phosphonates from readily available vinyl phosphates.[10] In this paper we describe this latter reaction in more detail, providing information on its mechanism, scope, and limitations.

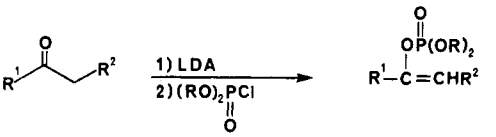
Scheme I



Scheme II



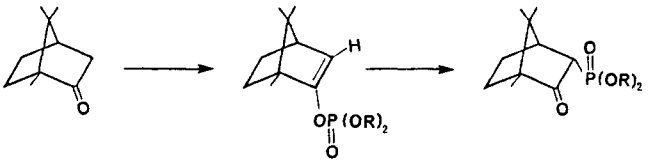
Scheme III



Results and Discussion

While the direct reaction of a dialkyl phosphorochloridate with an enolate results in the formation of a vinyl phosphate (Scheme III),[11] various 1,3-silicon migrations in similar systems[12] suggested that the vinyl phosphate itself could serve as a precursor to a β-keto phosphonate. Although this rearrangement would require breaking a P–O bond, it would result in the formation of a very stable keto phosphonate anion from a much less stable species.

To test this hypothesis, camphor (1) was treated sequentially with LDA and diethyl phosphorochloridate (at −78 °C in THF), to obtain the vinyl phosphate **2a**. When



1 2 a) R = Et b) R = i-Pr 3 a) R = Et b) R = i Pr

treated with LDA (−78 °C to room temperature), this vinyl phosphate rearranges smoothly to the β-keto phosphonate

(1) Fellow of the Alfred P. Sloan Foundation, 1985–87.

(2) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733. Horner, L.; Hoffman, H.; Wippell, H. G.; Klahre, G. *Chem. Ber.* **1959**, *92*, 2499. Horner, L.; Hoffman, H.; Klink, W.; Ertel, H.; Toscano, V. G. *Chem. Ber.* **1962**, *95*, 581. Wadsworth, W. S., Jr. *Org. React. (N.Y.)* **1977**, *25*, 73.

(3) For example, cf: (a) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405. (b) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. Blanchette, M. A.; Choy, W.; Davis, J. T.; Essenfeld, A. P.; Masamune, S.; Roush, W. R.; Sakai, T. *Tetrahedron Lett.* **1984**, *25*, 2183. Marshall, J. A.; DeHoff, B. S.; Cleary, D. G. *J. Org. Chem.* **1986**, *51*, 1735. (c) Sampson, P.; Roussis, V.; Drtina, G. J.; Koerwitz, F. L.; Wiemer, D. F. *J. Org. Chem.* **1986**, *51*, 2525.

(4) Arbuzov, B. A. *Pure Appl. Chem.* **1964**, *9*, 307. Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415.

(5) Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5654. Aboujaoude, E. E.; Collignon, N.; Savignac, P. *J. Organomet. Chem.* **1984**, *264*, 9. Mikolajczyk, M.; Balczewski, P. *Synthesis* **1984**, 691. Honda, M.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1984**, *25*, 3857. Coutrot, P.; Savignac, P.; Mathey, F. *Synthesis* **1978**, 36.

(6) Arbusov, B. A.; Vinogradova, V. S.; Polezhaeva, N. A. *Dokl. Akad. Nauk SSSR* **1961**, *137*, 855. Arbusov, B. A.; Vinogradova, V. S.; Polezhaeva, N. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, 71.

(7) Maslennikov, I. G.; Lavrent'ev, A. N.; Kuz'mina, N. Ya.; Kirichenko, L. N. *J. Gen. Chem. USSR* **1981**, *51*, 1329.

(8) Herzig, C.; Gasteiger, J. *Chem. Ber.* **1982**, *115*, 601.

(9) Sampson, P.; Hammond, G. B.; Wiemer, D. F. *J. Org. Chem.* **1986**, *51*, 4342.

(10) Hammond, G. B.; Calogeropoulou, T.; Wiemer, D. F. *Tetrahedron Lett.* **1986**, *27*, 4265.

(11) Lichtenthaler, F. U. *Chem. Rev.* **1961**, *61*, 607.

(12) Sampson, P.; Wiemer, D. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1746.

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3a in a reaction easily monitored by ^{31}P NMR ($\Delta\delta$ from −6.23 ppm to +23.07 ppm). While the intermediate vinyl phosphate is sufficiently stable to be isolated by distillation or chromatography, the β-keto phosphonate **3a** can be obtained directly by sequential treatment of camphor with LDA, $(EtO)_2P(O)Cl$, and LDA (71%). The conversion of camphor to its β-keto phosphonate is especially noteworthy because attempted synthesis of this compound by the Arbuzov reaction of α-bromocamphor with triethyl phosphite fails, and preparation of this phosphonate from a simple alkyl phosphonate (e.g., dimethyl methylphosphonate) would be an ambitious task.

This migration also is observed in other ring systems (Table I), yielding those β-keto phosphonates that are least accessible via other means. Isolated yields are very good, the starting materials are readily available, and the experimental protocol is simple. While vinyl phosphates of both five- and six-membered ring ketones readily undergo rearrangement, with cyclohexanone it was found advantageous to conduct the reaction at low temperature to minimize formation of side products. When this migration was attempted with the vinyl phosphate of cycloheptanone, a dimeric cycloheptene product[13] was formed. This suggests that the vinyl phosphates of larger ring ketones can undergo a phosphate elimination to an allene or alkyne, which may be followed by dimerization if the elimination product is strained.[14]

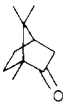
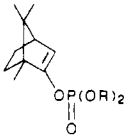
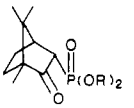
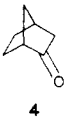
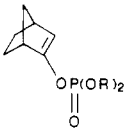
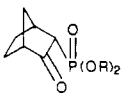
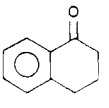
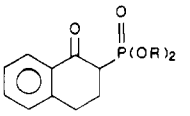
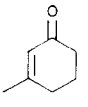
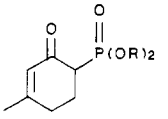
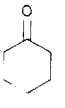
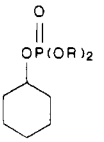
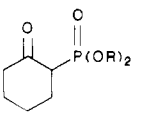
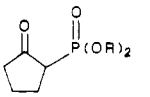
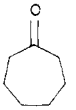
When enolates derived from acyclic ketones are treated under the same experimental conditions, the results are more complex. With methyl ketones such as acetophenone, a phosphate elimination resulting in alkyne formation[15] predominates under these experimental conditions. With more substituted acyclic ketones, e.g., 3-pentanone or propiophenone, more complicated product mixtures are obtained.

The nature of the phosphonate ester groups can affect the stereoselectivity of Wadsworth–Horner–Emmons reactions, with isopropyl esters often used to enhance trans stereoselectivity.[3b] Therefore we decided to determine if this migration could be used to prepare diisopropyl phosphonates directly from ketones via their vinyl phosphates. Treatment of this series of cyclic ketones (see Table I) with LDA, $((CH_3)_2CHO)_2P(O)Cl$,[16] and then LDA afforded the expected β-keto phosphonates in yields comparable to those obtained in the ethyl series.

To gain insight into the mechanism of this rearrangement, we have carried out several experiments. First of all, a simple crossover experiment was conducted, wherein a mixture of equimolar amounts of the diethyl vinyl phosphate of camphor (**2a**) and the diisopropyl vinyl phosphate of norcamphor (**5b**) was treated with LDA in THF. Careful analysis of the resulting reaction mixture revealed only the products of intramolecular migration (i.e., phosphonates **3a** and **6b**), suggesting that at least in this case the rearrangement is an intramolecular process.

A second line of experiments was conducted to establish the site of proton abstraction. With the vinyl phosphates of camphor and tetralone (Table I), an intramolecular rearrangement proceeding via formation of an anion can occur only by abstraction of the vinylic hydrogen. However, with ketones such as cyclohexanone, the migration might occur via abstraction of the vinylic hydrogen of the vinyl phosphate or via abstraction of a proton from the

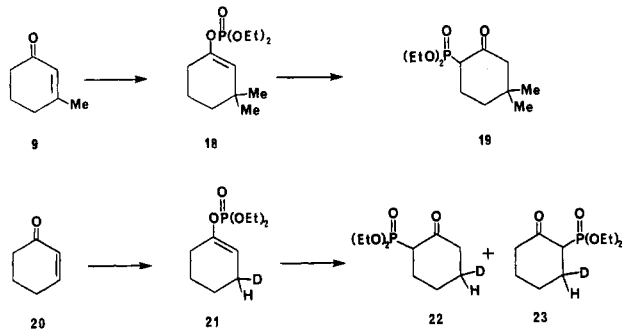
Table I. Synthesis of β-Keto Phosphonates

ketone	vinyl phosphate (isolated)	β-keto phosphonate	yield,[a] %
 1	 **2a**, R = Et	 **3a**, R = Et **3b**, R = *i*-Pr	72 80
 4	 **5b**, R = *i*-Pr	 **6a**, R = Et **6b**, R = *i*-Pr	85 75
 7		 **8a**, R = Et **8b**, R = *i*-Pr	88 70
 9		 **10a**, R = Et **10b**, R = *i*-Pr	75 80
 11	 **12a**, R = Et **12b**, R = *i*-Pr	 **13a**, R = Et **13b**, R = *i*-Pr	68[b] 76[b]
 14		 **15a**, R = Et **15b**, R = *i*-Pr	70 80
 16		(dimer[13]) 17	

[a] Isolated yield from ketone to β-keto phosphonate. [b] Isolated yield from ketone to β-keto phosphonate via isolated vinyl phosphate.

α′ position forming an intermediate allyl anion. To begin consideration of this question, the vinyl phosphate (**18**) was prepared by methyl cuprate addition to 3-methyl-2-cyclohexenone (**9**) and trapping of the resulting enolate with $(EtO)_2P(O)Cl$. Treatment of the vinyl phosphate **18** with LDA gave a single product, which was easily identified as **19** upon ^1H NMR analysis. In a similar experiment, cyclohexenone (**20**) was treated with $LiAlD_4/CuI$,[17] and the reduction product was trapped by reaction with diethyl phosphorochloridate to obtain the vinyl phosphate **21**. Treatment of the vinyl phosphate **21** with LDA gives phosphonates **22** and **23** in equal amounts, as indicated by analysis of the inverse gated decoupled ^{13}C NMR spectrum of the product mixture. The results of these experiments

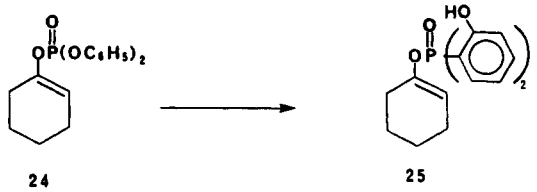
(13) Bottini, A. T.; Frost, K. A., II.; Anderson, B. R.; Dev, V. *Tetrahedron* **1973**, *29*, 1975.
(14) Price, J. D.; Johnson, R. P. *Tetrahedron Lett.* **1986**, *27*, 4679.
(15) Negishi, E.; King, A. O.; Klime, W. L.; Patterson, W.; Silveria, A. Jr. *J. Org. Chem.* **1980**, *45*, 2526.
(16) Sosnovsky, G.; Zaret, E. H. *J. Org. Chem.* **1969**, *94*, 968.
(17) Tsuda, T.; Fujii, T.; Kawasaki, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1013.



suggest that this rearrangement can occur via abstraction of an allylic hydrogen where one is available and that phosphorus migration can occur to either terminus of an allyl anion. Furthermore, with vinyl phosphates where formation of an allyl anion is possible, the regiochemistry of the rearrangement may not be controlled by the regiochemistry observed in formation of the vinyl phosphate but by steric and/or electronic factors in the vinyl phosphate anion. As noted above, however, phosphorus migration to the vinylic position also can occur when formation of an allyl anion is precluded.

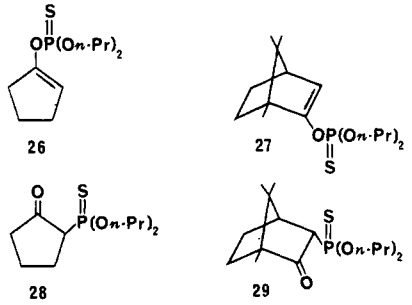
Finally, with the deuteriated compound **21** in hand, it was possible to conduct a more sophisticated crossover experiment. When an equimolar mixture of the vinyl phosphates **21** and **12b** was treated with LDA in THF, again only the products of intramolecular rearrangement were observed (**22**/**23** and **13b**). This finding suggests that those rearrangements which proceed via formation of allyl anions also are intramolecular reactions.

There is precedent for an anionic rearrangement of vinyl phosphates in the recent work of Dhawan and Redmore,[18] who reported that triphenyl phosphates undergo rearrangement to bis(2-hydroxyaryl)phosphinates upon treatment with strong base. To test the viability of synthesis of diphenyl β-keto phosphonates via rearrangement of a diphenyl vinyl phosphate, we performed an internal "competition" experiment. When the diphenyl vinyl phosphate of cyclohexanone (**24**) was treated with LDA,



migration of phosphorus from oxygen to the aromatic ring was observed, producing compound **25**. Therefore we conclude that rearrangement of phosphorus to the ortho position of a phenyl ring can take precedence over rearrangement to either vinylic or allylic positions.

Finally, a number of thiophosphonates are of interest as agricultural chemicals, and preliminary experiments indicate that this general protocol can be used to prepare thiophosphonates. Using commercially available di-*n*-propyl thiophosphorochloridate, the vinyl thiophosphates of cyclopentanone and camphor were prepared (compounds **26** and **27**). Upon attempted rearrangement, the corresponding β-keto thiophosphonates **28** and **29** were obtained in good yields (78% and 82%, respectively). These migrations are considerably slower than their phosphate analogues, even if higher temperatures and more equivalents of base are employed, for reasons not yet



completely understood. It is possible that complexation between vinyl phosphate oxygen(s) and the lithium base facilitates anion formation in vinyl phosphates,[19] and thus speeds the rearrangement vis-a-vis the analogous vinyl thiophosphates.

In conclusion, this new procedure for the preparation of β-keto phosphonates works well with cyclic compounds, providing ready access to structures previously available only via lengthy custom syntheses. Further extensions of this methodology, and new applications of the resulting products, will be reported in due course.

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Flash column chromatography was done on Merck grade 60 silica gel (230–400 mesh), while radial chromatography was done with a Chromatotron apparatus using Merck PF254 silica gel with $CaSO_4 \cdot 0.5H_2O$. The IR spectra were recorded on an IBM Model 98 FT IR instrument. NMR spectra (^1H, ^2H, ^{13}C, and ^{31}P) were recorded on either a JEOL FX-90Q or a Brucker WM-360 spectrometer, using deuteriochloroform as the solvent (chloroform for ^2H spectra). The ^1H and ^{13}C chemical shifts are reported in parts per million downfield from $(CH_3)_4Si$, while the ^{31}P chemical shifts are reported in parts per million relative to H_3PO_4 (external standard). Low resolution electron impact (EI) mass spectra were recorded with a Hewlett-Packard 5985B instrument operating at 70 eV; only selected ions are reported here. High resolution mass spectra were recorded on a Kratos MS-50 instrument at the Midwest Center for Mass Spectrometry. Microanalyses were conducted by MicAnal Laboratories, Tucson, AZ. Standard workup refers to a procedure where a solution of acetic acid in diethyl ether (1 M, 4 equiv) is added slowly to the cooled reaction mixture, and the resulting mixture is filtered through a Florisil (60–120 mesh) pad.

3-(Diethoxyphosphinyl)camphor (3a). General Procedure for the Preparation of Diethyl β-Keto Phosphonates. A solution of camphor (0.37 g, 2.43 mmol) in anhydrous THF (4 mL) was added dropwise via syringe to a stirred solution of lithium diisopropylamide [LDA, 1.1 equiv, prepared in situ from diisopropylamine (0.38 mL) and *n*-BuLi (1.71 mL, 1.60 M)] in THF (1.5 mL) at −65 °C. After 45 min, the resulting enolate was treated with diethyl phosphorochloridate (0.4 mL, 2.67 mmol) and the mixture was allowed to warm to 0 °C over the course of 50 min. After this mixture was cooled to −75 °C, it was transferred to a solution of LDA (2.2 equiv in 3 mL of THF). The resulting solution was allowed to warm to 10 °C over 2 h. Standard workup followed by concentration of the filtrate gave the desired product **3a** (500 mg, 71%). An analytically pure sample was obtained by Kugelrohr distillation. Anal. Calcd for $C_{14}H_{25}O_4P$: C, 58.32; H, 8.74. Found: C, 58.17; H, 8.97.

3-(Diethoxyphosphinyl)-2-norbornanone (6a). A solution of 2-norbornanone (0.55 g, 5.0 mmol) in THF (5 mL) was treated sequentially with LDA (1.1 equiv) in THF (5 mL), diethyl phosphorochloridate (0.8 mL, 5.5 mmol), and LDA (2.3 equiv) in THF (6 mL) by using the general procedure described above. The reaction mixture was allowed to warm to 10 °C during the course of 2.5 h and then was worked up as above, yielding the phosphonate **6a** (1.05 g, 85%). Purification by column chroma-

(18) Dhawan, B.; Redmore, D. *J. Org. Chem.* **1984**, *49*, 4018. Dhawan, B.; Redmore, D. *J. Org. Chem.* **1986**, *51*, 179.

(19) Beak, P.; Hunter, J. E.; Jun, Y. M. *J. Am. Chem. Soc.* **1983**, *105*, 6350. Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080. Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

tography (silica gel; 50% EtOAc, 50% hexane) produced an analytically pure sample (962 mg). Anal. Calcd for $C_{11}H_{19}O_4P$: C, 53.65; H, 7.78. Found: C, 53.90; H, 7.98.

2-(Diethoxyphosphinyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (8a). Treatment of 1-oxo-1,2,3,4-tetrahydronaphthalene (0.4 mL, 3 mmol) with a solution of LDA (1.1 equiv) in THF (7 mL) at −60 °C was followed by addition of diethyl phosphorochloridate (0.55 mL, 3.6 mmol) and LDA (2.2 equiv in 8 mL of THF) according to the general procedure. Gradual warming (to −20 °C over the course of 1 h) and standard workup produced compound **8a** (735 mg, 88%): bp 127–129 °C (0.15 mmHg). Anal. Calcd for $C_{14}H_{19}O_4P$: C, 59.57; H, 6.78. Found: C, 59.15; H, 6.93.

6-(Diethoxyphosphinyl)-3-methylcyclohex-2-en-1-one (10a). 3-Methylcyclohex-2-en-1-one (0.58 mL, 5 mmol) was treated sequentially with LDA (1.1 equiv in 10 mL of THF), diethyl phosphorochloridate (0.8 mL, 5.5 mmol), and LDA (2.3 equiv in 6 mL of THF) in a manner analogous to the general procedure. After 0.5 h, standard workup followed by purification by column chromatography (silica gel, 70% EtOAc, 30% hexane) gave the desired phosphonate **10a** (935 mg, 75%). Anal. Calcd for $C_{11}H_{19}O_4P$: C, 53.65; H, 7.78. Found: C, 53.51; H, 7.84.

2-(Diethoxyphosphinyl)cyclohexanone (13a). Cyclohexanone (0.52 mL, 5 mmol) was treated with LDA (1.1 equiv in 10 mL of THF), and the resulting anion was trapped by reaction with diethyl phosphorochloridate (0.8 mL, 5.5 mmol). Workup with NH_4Cl gave the expected vinyl phosphate **12a** (1.11 g, 95%): ^1H NMR δ 5.49–5.47 (m, 1, olefinic H), 4.19–4.11 (m, 4, OCH_2CH_3), 2.22–2.18 (m, 2, CH_2), 2.10–2.05 (m, 2, CH_2), 1.75–1.68 (m, 2, CH_2), 1.58–1.53 (m, 2, CH_2), 1.37–1.32 (m, 6, OCH_2CH_3); ^{31}P NMR −6.1; GCMS, m/z (rel intensity) 234 (M^+, 11), 206 (6), 177 (10), 127 (33), 109 (9), 99 (100), 97 (19), 81 (37), 80 (39), 79 (58), 55 (12), 41 (10). This vinyl phosphate (246 mg, 1.05 mmol in 10 mL of THF) was added dropwise to a solution of LDA (2.2 equiv in 6 mL of THF) at −90 °C. After 3.5 h at −90 °C, standard workup and purification by column chromatography (silica gel, 50% EtOAc, 50% hexane) gave the keto phosphonate **13a** (177 mg, 72%).[8]

2-(Diethoxyphosphinyl)cyclopentanone (15a). Compound **15a** was prepared from cyclopentanone (0.44 mL, 5 mmol) by a sequence analogous to that described above for compound **10a**. Standard workup and purification by radial chromatography (silica gel, 80% EtOAc, 20% hexane) furnished phosphonate **15a** (750 mg, 70%): HRMS, calcd for $C_9H_{17}O_4P$ 220.0865, found 220.0858.

3-(Diisopropoxyphosphinyl)camphor (3b). General Procedure for the Preparation of Diisopropyl β-Keto Phosphonates. A solution of camphor (0.76 g, 5.0 mmol) in anhydrous THF (4 mL) was added dropwise via syringe to a stirred solution of LDA (1.1 equiv, prepared in situ from diisopropylamine (0.77 mL) and *n*-BuLi (2.4 mL, 2.5 M)), in THF (6 mL) at −65 °C. After 45 min, the resulting enolate was treated with diisopropyl phosphorochloridate[16] (1.0 mL, 5.5 mmol) and the resulting mixture was allowed to warm to 0 °C during the course of 50 min. It was then cooled to −75 °C and transferred to a solution of LDA (2.3 equiv) in THF (6 mL). The reaction mixture was allowed to warm to 10 °C over 2 h. Standard workup followed by concentration of the filtrate gave the desired product **3b** (1.28 g, 80%). An analytically pure sample was obtained by flash chromatography (silica gel, 50% EtOAc, 50% hexane). Anal. Calcd for $C_{16}H_{29}O_4P$: C, 60.74; H, 9.24. Found: C, 60.70; H, 9.54.

3-(Diisopropoxyphosphinyl)-2-norbornanone (6b). Treatment of 2-norbornanone (0.55 g, 5 mmol) with LDA, diisopropyl phosphorochloridate, and LDA as described above gave, after standard workup and column chromatography (silica gel, 50% EtOAc, 50% hexane), compound **6b** (0.964 g, 75%): HRMS, calcd for $C_{13}H_{23}O_4P$ 274.1335, found 274.1332.

2-(Diisopropoxyphosphinyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (8b). Application of the general procedure given above with α-tetralone (0.66 mL, 5.0 mmol) resulted in the formation of the expected phosphonate. Purification by column chromatography (silica gel, 15% EtOAc, 85% hexane) gave pure compound **8b** (1.09 g, 70%). Anal. Calcd for $C_{16}H_{23}O_4P$: C, 61.93; H, 7.47. Found: C, 61.40; H, 7.42.

6-(Diisopropoxyphosphinyl)-3-methylcyclohex-2-en-1-one (10b). When the general procedure described above was used with 3-methylcyclohex-2-en-1-one (0.58 mL, 5 mmol) migration was complete after 40 min. Standard workup and column chromatography (silica gel, 50% EtOAc, 50% hexane) gave the expected phosphonate **10b** (1.10 g, 80%). Anal. Calcd for $C_{13}H_{23}O_4P$: C, 56.93; H, 8.45. Found: C, 56.97; H, 8.74.

2-(Diisopropoxyphosphinyl)cyclohexanone (13b). Treatment of cyclohexanone (1.04 mL, 10 mmol) with LDA and diisopropyl phosphorochloridate (2.1 mL, 11 mmol) in a manner analogous to that described above for preparation of the diethyl phosphate of cyclohexanone, gave the expected vinyl phosphate **12b** (2.270 g, 87%): ^1H NMR δ 5.49–5.47 (m, 1, olefinic H), 4.72–4.63 (m, 2, $OCH(CH_3)_2$), 2.21–2.17 (m, 2, CH_2), 2.10–2.05 (m, 2, CH_2), 1.74–1.67 (m, 2, CH_2), 1.58–1.51 (m, 2, CH_2), 1.36–1.29 (m, 12, $OCH(CH_3)_2$); ^{31}P NMR −7.8; GCMS, m/z (rel intensity) 262 (M^+, 6), 220 (4), 178 (100), 150 (5), 107 (11), 99 (62), 97 (22), 80 (72), 79 (46), 43 (18), 40 (89). This vinyl phosphate (276 mg, 1.05 mmol in 10 mL of THF) was added dropwise to a solution of LDA (2.2 equiv in 6 mL of THF) at −90 °C. After 4 h at −90 °C, standard workup and purification by column chromatography gave the keto phosphonate **13b** (221 mg, 80%). Anal. Calcd for $C_{12}H_{23}O_4P$: C, 54.95; H, 8.84. Found: C, 54.96; H, 9.09.

2-(Diisopropoxyphosphinyl)cyclopentanone (15b). The title compound was prepared from cyclopentanone (0.44 mL, 5 mmol) according to the general procedure. After 1.5 h the migration was complete. Standard workup followed by purification by column chromatography (silica gel, 50% EtOAc, 50% hexane) gave the expected phosphonate **15b** (990 mg, 80%). Anal. Calcd for $C_{11}H_{21}O_4P$: C, 53.22; H, 8.43. Found: C, 53.06; H, 8.66.

Attempted Preparation of Cycloheptanone Phosphonate. A solution of cycloheptanone (0.3 mL, 2.5 mmol) in THF (3.5 mL) was treated sequentially with LDA (1.1 equiv in 3.5 mL of THF), diethyl phosphorochloridate (0.4 mL, 2.8 mmol), and LDA (3 equiv in 9 mL of THF) by using our standard procedure. The reaction mixture was allowed to warm to −30 °C during the course of 30 min and then was quenched with saturated NH_4Cl. After the organic layer was removed, the aqueous layer was extracted with ether (1 × 25 mL) and the combined organic layers were washed with saturated NH_4Cl (2 × 25 mL), dried, and concentrated. The residual oil was purified by distillation in vacuo to give cycloheptene dimer **17** (182 mg, 77%): bp 85–90 °C/0.1 mmHg; ^1H NMR δ 5.71 (t, 2, J = 4.4 Hz, olefinic H), 2.6–0.8 (m, 18); ^{13}C NMR 145.8, 118.1, 48.6, 33.2, 30.8, 29.7, 28.8, 22.6; GCMS, m/z (rel intensity) 188 (M^+, 16), 173 (8), 159 (13), 145 (37), 131 (46), 119 (20), 117 (46), 105 (38), 91 (100), 77 (45).[13]

2-[(Diethoxyphosphinyl)oxy]-1,7,7-trimethylbicyclo[2.2.1]-2-heptene (2a). A solution of camphor (0.76 g, 5 mmol) in THF (5 mL) was added to LDA (1.1 equiv in 5 mL of THF) at −78 °C. After the solution was stirred for 0.5 h, diethyl phosphorochloridate (0.8 mL, 5.5 mmol) was added. The mixture was allowed to warm up to room temperature over 1.5 h before it was quenched by the addition of saturated NH_4Cl. After the organic layer was removed, the aqueous layer was extracted with ether (1 × 25 mL) and the combined organic fractions were dried ($MgSO_4$) and concentrated in vacuo to afford vinyl phosphate **2a** (1.46 g, 100%): bp 90–92 °C/0.15 mmHg; IR 1624 cm^{-1} (C=C); ^1H NMR δ 5.31 (d, 1, J = 3.5 Hz, olefinic H), 4.20–4.12 (m, 4, OCH_2CH_3), 2.31 (t, 1, J = 3.5 Hz, CH), 1.89–1.12 (m, 4, CH_2's), 1.35 (dt, 6, J_{HP} = 1.1 Hz, J = 7.1 Hz, OCH_2CH_3), 0.97, 0.90, 0.75 (each s, 3, CH_3's); ^{31}P NMR −6.06; GC MS, m/z (rel intensity) 288 (M^+, 5), 260 (16), 189 (13), 155 (31), 127 (26), 119 (60), 106 (100), 99 (32), 91 (78), 81 (40); HRMS, calcd for $C_{14}H_{25}O_4P$ 288.1491, found 288.1489.

2-[(Diisopropoxyphosphinyl)oxy]bicyclo[2.2.1]-2-heptene (5b). Treatment of 2-norbornanone (0.55 g, 5 mmol) with a reaction sequence analogous to that described above for preparation of the vinyl phosphate of camphor gave compound **5b** (1.35 g, 100%): ^1H NMR δ 5.28 (br s, 1, olefinic H), 4.73–4.60 (m, 2, $OCH(CH_3)_2$), 2.86–2.84 (m, 2, CH's), 1.77–1.33 (m, 18); ^{31}P NMR −8.2; GCMS, m/z (rel intensity) 274 (M^+, 1), 204 (7), 162 (85), 123 (6), 99 (8), 91 (22), 82 (45), 43 (100), 41 (60).

Attempted Crossover Experiment with Compounds 2a and 5b. A mixture of the diethyl phosphate of camphor (**2a**, 0.25 g, 0.86 mmol), and the diisopropyl phosphate of norcamphor (**5b**, 0.24 g, 0.87 mmol) was treated with LDA (4.5 mmol) in the usual manner. After standard workup only keto phosphonates **3a** and **6b** were observed by GC and GCMS (in comparison with authentic samples).

Table II. Spectral Data for β-Keto Phosphonates

cmpd	^1H, ^{31}P, and ^{13}C NMR data, ppm	MS data, m/z (rel intensity)
3a	4.32–4.07 (m, 4), 2.93 (dd, 1, J_{HP} = 13.5 Hz, J = 5 Hz, CHP(O)), 2.40–1.45 (m, 5), 1.34 (t, 6, J = 7 Hz), 1.00, 0.92, 0.86 (each s, 3); +23.1; 211.5, 62.1 (d, J = 6 Hz), 59.0 (d, J = 3 Hz), 50.8 (d, J = 144.1 Hz), 47.0 (d, J = 17.4 Hz), 46.3, 29.8, 23.1 (d, J = 4.7 Hz), 19.5, 18.9, 16.5 (d, J = 6.1 Hz), 9.8	288 (M^+, 16), 260 (42), 178 (77), 152 (100), 123 (69), 109 (65), 91 (65), 81 (75)
6a	4.25–4.10 (m, 4), 3.00–2.94 (m, 1, CHP(O)), 2.71–2.64 (m, 1), 2.45–2.35 (m, 1), 1.91–1.20 (m, 12); +21.70, +20.36 (two diastereomers)	246 (M^+, 33), 218 (54), 190 (100), 162 (86), 152 (90), 134 (46), 109 (41), 91 (30), 81 (77)
8a	8.1–7.2 (m, 4), 4.3–4.0 (m, 4), 3.5–2.2 (m, 5), 1.5–1.1 (m, 6); +22.9; 192.4 (d, J = 5.7 Hz), 143.8, 133.7, 132.2 (d, J = 2.4 Hz), 128.7, 127.6, 126.7, 62.5 (d, J = 6.7 Hz), 62.3 (d, J = 6.2 Hz), 47.3 (d, J = 124 Hz), 27.5 (d, J = 7.3 Hz), 24.4 (d, J = 4.5 Hz), 16.3 (d, J = 6 Hz)	282 (M^+, 7), 225 (8), 144 (100), 127 (15), 115 (55), 90 (20), 81 (11)
10a	5.91 (s, 1), 4.19–4.08 (m, 4), 2.94 (dt, 1, J_{HP} = 25.3 Hz, J = 5.6 Hz, CHP(O)), 2.7–2.2 (m, 4), 1.99 (s, 3), 1.36–1.28 (m, 6); +23.6	246 (M^+, 3), 201 (6), 189 (9), 165 (8), 138 (70), 111 (79), 108 (100), 91 (14), 82 (30)
13a[8]	8.2 (s, enol OH), 4.20–3.99 (m, 4), 2.97 (dt, 1, J_{HP} = 23.4 Hz, J = 5.1 Hz, CHP(O)), 2.68–1.66 (m, 8), 1.35–1.30 (m, 6); +23.67, +27.43 (keto–enol tautomerism)	234 (M^+, 34), 206 (37), 178 (37), 150 (42), 139 (58), 138 (100), 137 (40), 111 (82), 109 (63), 96 (50), 81 (60)
15a[6]	4.2–3.9 (m, 4), 3.0–1.8 (m, 7), 1.34 (t, 6, J = 7 Hz); +22.7	220 (M^+, 15), 192 (7), 165 (39), 137 (46), 109 (100), 82 (54), 65 (11)
3b	4.88–4.74 (m, 2), 2.93 (ddd, 1, J_{HP} = 27.6 Hz, J = 4.3, 2.2 Hz, CHP(O)), 2.33 (t, 1, J = 4.2 Hz), 2.14–1.61 (m, 4), 1.38–1.30 (m, 12), 0.99, 0.91, 0.85 (each s, 3); +20.9	316 (M^+, 3), 274 (3), 246 (5), 232 (11), 204 (29), 189 (12), 150 (18), 135 (16), 122 (67), 109 (41), 55 (35), 43 (100)
6b	4.86–4.68 (m, 2), 2.97–2.91 (m, 1, CHP(O)), 2.68–2.59 (m, 1), 2.41–2.38 (m, 1), 1.90–1.23 (m, 18); +19.67, +18.18 (two diastereomers)	274 (M^+, 3), 233 (8), 217 (15), 191 (38), 190 (33), 162 (49), 123 (31), 109 (25), 80 (49), 43 (100)
8b	8.0–7.2 (m, 4), 4.82–4.62 (m, 2), 3.34–3.26 (m, 1, C*H*CHP(O)), 3.16 (dt, 1, J_{HP} = 26 Hz, J = 5.7 Hz, CHP(O)), 2.9–2.3 (m, 3), 1.40–1.20 (m, 12); +20.4	310 (M^+, 5), 268 (5), 226 (43), 209 (12), 144 (100), 127 (12), 115 (39), 90 (11)
10b	5.91 (s, 1), 4.78–4.65 (m, 2), 2.85 (dt, 1, J_{HP} = 25.4 Hz, J = 5.4 Hz, CHP(O)), 2.72–2.16 (m, 4), 1.96 (s, 3), 1.38–1.19 (m, 12); +23.8	274 (M^+, 0.3), 232 (1), 190 (8), 173 (9), 124 (2), 109 (25), 108 (100), 91 (7), 82 (14)
13b	4.81–4.55 (m, 2), 2.91 (dt, 1, J_{HP} = 24 Hz, J = 4.9 Hz CHP(O)), 2.71–2.62 (m, 1), 2.4–1.6 (m, 7), 1.38–1.29 (m, 12); +25.0, +21.5 (keto–enol tautomerism); 206.2 (d, J = 4.0 Hz), 70.9 (d, J = 7 Hz), 51.2 (d, J = 132 Hz), 41.5, 28.1 (d, J = 4.9 Hz), 26.7, 23.8 (d, J = 5.3 Hz), 22.4 (d, J = 4.7 Hz)	262 (M^+, 6), 220 (9), 178 (100), 161 (29), 150 (63), 122 (71), 109 (30), 96 (81), 83 (31), 79 (34), 41 (80)
15b	4.80–4.68 (m, 2), 2.67 (dt, 1, J_{HP} = 26.3 Hz, J = 7.4 Hz, CHP(O)), 2.39–1.83 (m, 6), 1.39–1.29 (m, 12); +20.6	248 (M^+, 3), 206 (5), 191 (20), 164 (71), 147 (23), 136 (10), 109 (69), 91 (9), 83 (33), 82 (100), 55 (22), 43 (24)

Vinyl Phosphate 18. A solution of ketone **9** (0.17 mL, 1.5 mmol) in ether (20 mL) was added dropwise to an ether solution of lithium dimethylcuprate (prepared in situ from copper(I) iodide (0.38 g, 2 mmol) and MeLi (4 mmol)) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C prior to the addition of diethyl phosphorochloridate (1.7 mL, 11.5 mmol). After 45 min at room temperature, standard workup and purification by flash chromatography (silica gel, 60% hexane, 40% EtOAc) gave phosphate **18** (0.25 g, 65%): ^1H NMR δ 5.25 (br s, 1, olefinic H), 4.30–3.97 (m, 4, OCH_2CH_3), 2.35–1.1 (m, 12), 1.01 (s, 6, CH_3's); ^{31}P NMR −6.5; GCMS, m/z (rel intensity) 262 (M^+, 8), 247 (58), 219 (16), 191 (12), 155 (23), 127 (35), 111 (37), 99 (100), 93 (79), 81 (96), 55 (75), 41 (58).

3,3-Dimethyl-6-(diethoxyphosphinyl)cyclohexanone (19). The vinyl phosphate **18** (0.13 g, 0.48 mmol) in THF (2 mL) was added dropwise to an LDA solution (2.4 equiv in 0.5 mL of THF) at −78 °C, and the resulting mixture was allowed to warm to room temperature during the course of 1 h. Standard workup, followed by column chromatography (silica gel, 50% EtOAc, 50% hexane), yielded phosphonate **19** (102 mg, 80%): ^1H NMR δ 4.21–4.02 (m, 4, OCH_2CH_3), 2.90 (dt, 1, J_{HP} = 23.1 Hz, J = 5.8 Hz, CHP(O)), 2.50 (dd, 1, J = 13.5, 2.2 Hz, CHC(O)), 2.24–1.90 (m, 5, CH_2's, CHC(O)), 1.36–1.30 (m, 6, OCH_2CH_3), 1.02, 0.96 (each s, 3, CH_3); ^{31}P NMR +23.2; GCMS, m/z (rel intensity) 262 (M^+, 25), 247 (75), 234 (40), 219 (50), 191 (60), 178 (75), 165 (55), 138 (100), 109 (80), 81 (50); HRMS, calcd for $C_{11}H_{20}O_4P$ 247.1104 (M^+ − 15), found 247.1097.

Vinyl Phosphate 21. A slurry of Cu(I)I (381 mg, 2 mmol) in THF/HMPA (2 mL of each) was added to a suspension of $LiAlD_4$ (84 mg, 2 mmol in 6 mL of THF, 98% D) at −78 °C. After the resulting mixture was stirred for 30 min (−78 °C), 2-cyclohexen-1-one (0.19 mL, 2 mmol) was added. After 1 h at −78 °C, diethyl phosphorochloridate (1.6 mL, 11 mmol) was added, and the resulting vinyl phosphate was isolated after addition of NH_4Cl and column chromatography (315 mg, 67%): ^1H NMR δ 5.48–5.47 (m, 1, olefinic H), 4.20–4.10 (m, 4, OCH_2CH_3), 2.20–2.17 (m, 2, CH_2), 2.06–2.05 (m, 1, CHD), 1.75–1.68 (m, 2, CH_2), 1.57–1.52 (m, 2, CH_2), 1.38–1.33 (m, 6, OCH_2CH_3); ^{31}P NMR −6.1; ^{13}C NMR (^1H broadband decoupled) 147.6 (d, J = 8.8 Hz), 100.4 (d, J = 5.3 Hz), 63.95 (d, J = 6.0 Hz), 27.6 (d, J = 4 Hz), 23.2 (t, J = 19.5 Hz), 22.6, 21.5, 16.0 (d, J = 7 Hz); GCMS, m/z (rel intensity) 235 (M^+, 18), 207 (10), 178 (15), 128 (10), 127 (41), 100 (25), 99 (100), 81 (60), 80 (54). Analysis of the mass spectrum indicated 100% deuterium incorporation, while the ^2H NMR spectrum contained a single resonance (^2H NMR δ 2.05).

Migration of Vinyl Phosphate 21. The vinyl phosphate **21** (235 mg, 1.00 mmol in 10 mL of THF) was added dropwise to a solution of LDA (2.2 equiv in 6 mL of THF) at −90 °C. After 3.5 h at −90 °C, standard workup and purification by column chromatography gave the keto phosphonates **22** and **23** (150 mg, 65%). The ^1H NMR spectrum was generally indistinguishable from that reported for **13a** in Table II, except for the CHP(O) resonance. This signal appeared as a six-line pattern: a doublet of triplets (the resonance from the δ-deuterio isomer **22**, coupled to phosphorus and 2 adjacent H's) overlapping a doublet of doublets (the resonance from the β-deuterio isomer **23**, coupled to phosphorus and 1 adjacent H): ^{31}P NMR +27.4, +23.7 (keto enol tautomerism); ^{13}C NMR (^1H broadband decoupled) 206.0 (d, J = 5 Hz), 62.4 (d, J = 7.2 Hz), 62.3 (d, J = 7.1 Hz), 50.4 (d, J = 132.3 Hz), 50.3 (d, J = 132.8 Hz), 41.6 (d, J = 6.9 Hz), 27.9 (d, J = 5.0 Hz), 27.4 (dt, J = 20.0, 5.8 Hz), 26.5, 26.2 (t, J = 19.8), 22.5 (d, J = 5.9 Hz), 16.3 (d, J = 5.9 Hz); GCMS, m/z (rel intensity) 235 (M^+, 37), 207 (42), 179 (39), 178 (46), 151 (28), 139 (53), 138 (100), 111 (80), 110 (50), 109 (30), 97 (37), 83 (22), 82 (31). In an NOE suppressed, broadband decoupled ^{13}C NMR spectrum, the intensity of the signals at 26.5 and 26.2 ppm showed a 50:50 ratio for the two isomers **23** (in which this peak is a singlet) and **22** (in which this peak appears as a triplet). This isomer ratio

was confirmed by integration of the peaks at 27.9 (**22**) and 27.4 ppm (**23**).

Attempted Crossover Experiment with Compounds 21 and 12b. A mixture of the deuteriated diethyl phosphate **21** (58 mg, 0.25 mmol) and the diisopropyl phosphate **12b** (65.5 mg, 0.25 mmol) was treated with LDA (1.13 mmol) at −85 °C. After standard workup, only keto phosphonates **22**/**23** and **13b** were observed by GC and GCMS (in comparison with authentic samples).

Diphenyl Vinyl Phosphate 24. Addition of cyclohexanone (0.28 mL, 2.7 mmol) to a solution of LDA (1.1 equiv in 5 mL of THF) at −60 °C and stirring for 15 min was followed by addition of diphenyl phosphorochloridate (0.4 mL, 2.75 mmol). The resulting solution was stirred for 1 h, followed by the usual workup, to obtain the vinyl phosphate **24** (361 mg, 80%): ^{1}H NMR δ 7.2 (m, 10, aromatic H's), 5.5 (m, 1, olefinic H), 2.3–1.1 (m, 8, CH_2's); ^{31}P NMR −17.6; GCMS, m/z (rel intensity) 330 (M^+, 34), 251 (28), 233 (100), 215 (22), 168 (22), 157 (20), 139 (16), 94 (95), 79 (22), 77 (32).

1-Cyclohexenyl Bis(2-hydroxyphenyl)phosphinate (25). Vinyl phosphate **24** (0.16 g, 0.5 mmol) was treated with LDA (2.2 equiv in 3 mL of THF) at −78 °C, and the reaction mixture then was allowed to warm to room temperature over the course of 100 min. Aqueous workup using saturated NH_4Cl gave the phosphonate **25** (140 mg, 90%): ^{1}H NMR δ 9.9 (br s, 2, OH), 7.42–6.93 (m, 8, aromatic H's), 5.54 (br s, 1, olefinic H), 2.3–1.1 (m, 8, CH_2's); ^{31}P NMR +40.76; ^{13}C NMR 162.1 (d, J = 5.2 Hz), 147.5 (d, J = 10.2 Hz), 135.3, 131.5 (d, J = 7.6 Hz), 119.7 (d, J = 12.9 Hz), 118.4 (d, J = 8.9 Hz), 113.1 (d, J = 5.9 Hz), 111.4 (d, J = 140.3 Hz), 28.5 (d, J = 2.7 Hz), 23.7, 22.7, 21.4; GCMS, m/z (rel intensity) 330 (M^+, 32), 234 (53) 233 (100), 215 (54), 168 (47), 139 (30), 94 (47), 77 (26). Anal. Calcd for $C_{18}H_{19}O_4P$: C, 65.45; H, 5.80. Found: C, 65.35; H, 5.97.

Vinyl Thiophosphate 26. The anion of cyclopentanone (1.76 mL, 20 mmol) was generated by treatment with LDA (1.5 equiv in 30 mL of THF) at −70 °C. Di-*n*-propyl thiophosphorochloridate (4.8 mL, 24 mmol) was added at −60 °C and the resulting mixture was allowed to warm to room temperature and then heated at reflux overnight. Standard workup and purification by column chromatography (silica gel, 99% hexane, 1% EtOAc) gave compound **26** (4.44 g, 85%): ^{1}H NMR δ 5.27–5.25 (m, 1, olefinic H), 4.09–4.03 (m, 4, P(S)OCH_2), 2.47–2.43 (m, 2, CH_2), 2.36–2.31 (m, 2, CH_2), 1.96–1.89 (m, 2, CH_2), 1.77–1.67 (m, 4, P(S)OCH_2CH_2), 1.00–0.94 (m, 6, P(S)OCH_2CH_2CH_3); ^{31}P NMR +61.97; GCMS, m/z (rel intensity) 264 (M^+, 37), 222 (9), 180 (48), 115 (28), 99 (78), 98 (98), 83 (100), 67 (56), 66 (56), 43 (39).

2-(Di-*n*-propoxythiophosphinyl)cyclopentanone (28). The vinyl thiophosphate **26** (0.53 g, 2 mmol) was treated with LDA (4.8 equiv in 8 mL of THF) at −40 °C, and the resulting mixture was allowed to warm up to room temperature over 30 min. Heating at 60 °C for 3 h was followed by addition of saturated NH_4Cl. The aqueous layer was extracted with ether (2 × 20 mL) and the combined organic extracts were dried and concentrated. The residual oil was purified by column chromatography (silica gel, 99% hexane, 1% EtOAc) to afford phosphonate **28** (410 mg, 78%): ^{1}H NMR δ 4.15–3.94 (m, 4, P(S)OCH_2), 2.90 (dt, 1, J_{HP} = 23.8 Hz, J = 8.7 Hz, CHP(S)), 2.46–1.83 (m, 6, CH_2's), 1.73–1.64 (m, 4, P(S)OCH_2CH_2), 0.96 (t, 6, J = 7.4 Hz, P(S)OCH_2CH_2CH_3); ^{31}P NMR +91.2; GCMS, m/z (rel intensity) 264 (M^+, 1), 222 (3), 181 (23), 149 (5), 107 (9), 83 (22), 65 (11), 55 (24), 43 (81), 41 (100). Anal. Calcd for $C_{11}H_{21}O_3PS$: C, 50.00; H, 8.01. Found: C, 50.53; H, 8.29.

Vinyl Thiophosphate 27. Compound **27** was prepared from camphor (1.52 g, 10 mmol) in a manner analogous to the preparation of compound **26**. After standard workup, the vinyl thiophosphate **27** was obtained (3.28 g, 99%): ^{1}H NMR δ 5.32–5.30 (m, 1, olefinic H), 4.09–3.97 (m, 4, P(S)OCH_2), 2.31 (t, 1, J = 3.5 Hz, CH), 1.89–1.82 (m, 1, CH_2), 1.77–1.64 (m, 4, P(S)OCH_2CH_2), 1.58–1.01 (m, 3, CH_2's), 0.99–0.94 (m, 9, P(S)OCH_2CH_2CH_3, CH_3), 0.92, 0.75 (each s, 3, CH_3's); ^{31}P NMR +64.0; GCMS, m/z (rel intensity) 332 (M^+, 11), 304 (13), 247 (11), 205 (26), 134 (30), 119 (48), 115 (32), 107 (35), 106 (100), 91 (38).

3-(Di-*n*-propoxythiophosphinyl)camphor (29). The vinyl thiophosphate **27** (0.664 g, 2 mmol) was treated with LDA (4 equiv) in a manner similar to that described for compound **28**. Heating at 60 °C for 4.5 h followed by NH_4Cl workup provided, after purification by column chromatography (silica gel, 99% hexane 1% EtOAc), the thiophosphonate **29** (611 mg, 82%): ^{1}H NMR δ 4.19–3.94 (m, 4, P(S)OCH_2), 3.15 (ddd, 1, J_{HP} = 24.3 Hz, J = 2.2, 4.2 Hz, CHP(S)), 2.42 (t, 1, J = 4.2 Hz), 2.23–2.15 (m, 1), 1.88–1.82 (m, 1), 1.75–1.57 (m, 6, P(S)OCH_2CH_2, CH_2), 1.00–0.92 (m, 12, P(S)OCH_2CH_2CH_3, 2CH_3's), 0.86 (s, 3, CH_3); ^{31}P NMR +90.1; GCMS, m/z (rel intensity) 332 (M^+, 18), 290 (23), 249 (55), 220 (23), 151 (100), 150 (57), 139 (65), 122 (49), 109 (70), 41 (63). Anal. Calcd for $C_{16}H_{29}O_3PS$: C, 57.81; H, 8.79. Found: C, 58.03; H, 9.00.

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