A Facile Route to Allylic Phosphonates via Base-Catalyzed Isomerization of the Corresponding Vinyl Phosphonates

James J. Kiddle and James H. Babler*

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

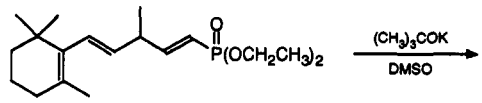
Received January 4, 1993

The past decade has seen a renewed interest in the synthesis of retinoids and carotenoids due in part to their diverse biological activity.[1] The major thrust of such synthetic efforts has been directed toward development of reliable methods for the synthesis of conjugated polyenes.

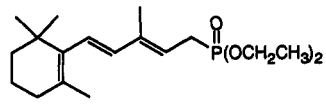
Phosphorus ylides are important reagents for the construction of carbon–carbon double bonds, most notably because their use affords control of the olefin regio- and stereoselectivity.[2] Among the various types of precursors to phosphorus ylides, allylic phosphonates have emerged as valuable synthetic intermediates in the preparation of dienes[3] and polyenes,[4] essential pivots in retinoid chemistry. A major advantage of allylic phosphonates over the corresponding phosphonium salts can be seen by the stereochemical outcome when each is used in Wittig-type reactions. Ylides derived from (*E*)-allylic phosphonium salts[5] react with carbonyl compounds to give a mixture of (*E*)- and (*Z*)-isomers[6] with respect to the newly generated olefinic linkage. Another stereochemical complication using such ylides is possible loss of stereochemical integrity in the olefinic functionality of the ylide.[7] In contrast, ylides derived from (*E*)-allylic phosphonates generally exhibit greater stereochemical control over olefin geometry.[2]

Unfortunately, some limitations exist in the classical route by which allylic phosphonates are prepared from allylic halides and a suitable trialkyl phosphite. In addition to a competing elimination, frequently during this Michaelis–Arbuzov reaction[8] allylic halides undergo allylic shifts with some loss of stereochemical integrity of the double bond. Although other methodologies exist for the synthesis of allylic phosphonates, they require the use of transition metal catalysts,[9] which may not be compatible with certain functional groups.

Recently,[10] one of us reported a novel synthesis of *all-trans*-retinoic acid, the key step of which involved isomerization of vinyl phosphonate **1** to the corresponding allylic phosphonate **2** (eq 1). *A priori*, this route did not seem feasible since the analogous allylic phosphonium salts are known to isomerize to the corresponding vinylphosphonium salts in the presence of base (i.e., the reverse of eq 1).[11] In addition, the isomerization of allylic phosphonates to vinyl phosphonates had been reported[12] using alkali metal hydroxides. The successful and novel isomerization of **1** to **2** prompted a further study of the scope of this methodology as a possible stereocontrolled approach to allylic phosphonates. Herein, we report the results of such a study.



1



2 (1)

Results and Discussion

The required vinyl phosphonates[13] were synthesized by a modified Wadsworth–Horner–Emmons olefination. Condensation of several representative carbonyl compounds (**3a-d**) with the anion derived from tetraethyl methylenediphosphonate (**4**)[14] afforded vinyl phosphonates **5a-d** in good yields (Table I). It is interesting to note that condensation of cyclohexanone (**3d**) with **4** affords only the exocyclic olefin **5d**. Previous attempts[15] to synthesize vinyl phosphonate **5d** demonstrated that the initial exocyclic double bond was readily isomerized to the endocyclic double bond.[16] The ^1H and ^{13}C NMR shift data and coupling constants were consistent with the structure **5d**, and the ^{31}P chemical shift obtained for **5d** (^{31}P δ 18.9) was in agreement with those obtained for vinyl phosphonates (**5a-c**) and other reported vinyl phosphonate ^{31}P chemical shifts.[17]

In an effort to maximize the yield of vinyl phosphonates **5a-d**, the condensation of isobutyraldehyde (**3a**) with tetraethyl methylenediphosphonate (**4**) was examined using several representative bases. As can be seen from the data in Table II, use of NaH in tetrahydrofuran afforded the highest yield of the desired product. Villieras and co-workers[18] have reported an 89% yield of **5a** using heterogeneous reaction conditions (K_2CO_3, H_2O, 100 °C) although we obtained only 38% using the same base in THF. Use of potassium carbonate in a more polar solvent such as DMSO, surprisingly, afforded a very poor yield (18%) of **5a**.

(1) Paust, J. *Pure Appl. Chem.* **1991**, *63*, 45–58 and references cited therein.
(2) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927.
(3) Warren, S.; Grayson, J. I.; Ernshaw, C.; Davidson, A. H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1452.
(4) Pattenden, G.; Weedon, B. C. L. *J. Chem. Soc., Chem. Commun.* **1968**, 1984, 1997.
(5) Maercker, A. *Org. React.* **1965**, *14*, 270.
(6) Crombie, L.; Hemesly, P.; Pattenden, J. *J. Chem. Soc., Chem. Commun.* **1969**, 1024.
(7) Schweizer, E. E.; Shaffer, E. T.; Hughes, C. T.; Berninger, C. J. *J. Org. Chem.* **1966**, *31*, 2907.
(8) For a review see: Bhattacharya, A. K.; Thyagarjan, G. *Chem. Rev.* **1981**, *81*, 415–430.
(9) For examples see: (a) Lu, X.; Zhu, J. *J. Organomet. Chem.* **1986**, *304*, 239–243. (b) Lu, X.; Zhu, J. *Tetrahedron Lett.* **1987**, *28*, 1897–1900. (c) Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 909–913.
(10) Babler, J. H.; Schlidt, S. A. *Tetrahedron Lett.* **1992**, *33*, 7697.
(11) Jacoby, D.; Celerier, J. P.; Petit, H.; Lhommet, G. *Synthesis* **1990**, 301 and refs 11–14 cited therein.
(12) Nalewajek, D.; Soriano, D. S. U.S. Patent 4 582 652, 1986.
(13) For a review of the synthesis of vinyl phosphonates see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333–349.
(14) Diphosphonate **4** can be purchased from Aldrich Chemical Co. or prepared from dibromomethane and triethyl phosphite according to a procedure described by: Czekanski, T.; Gross, H.; Costisella, B. J. *J. Prakt. Chem.* **1982**, *324*, 537.
(15) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939. Wysocki, D. C. PhD. Thesis, University of Pittsburgh, 1967.
(16) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.
(17) Tebby, J. C. *Phosphorus-31 NMR Spectroscopy in Strereochemical Analysis*; VCH Publishers: Florida, 1987; pp 1–60.
(18) Rambaud, M.; Vecchio, A.; Villieras, J. *Synth. Commun.* **1984**, *14*, 833–841.

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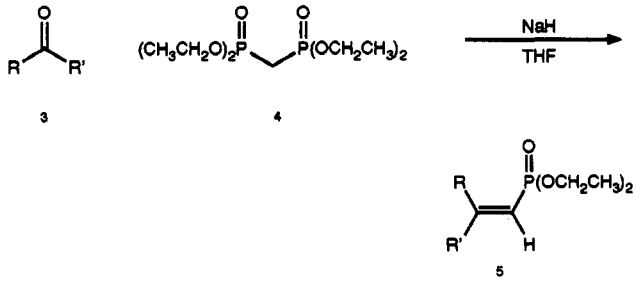
Table I. Synthesis of Vinyl Phosphonates



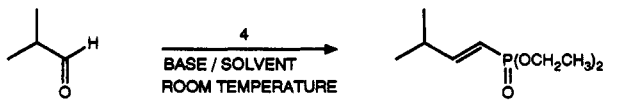
3 4 5

5a, R′ = $CH(CH_3)_2$; R = H
5b, R′ = CH_2Ph; R = H
5c, R′ = $(CH_2)_5CH_3$; R = H
5d, R′,R = $(CH_2)_5$

carbonyl compd	yield of 5 (%)	^{31}P NMR δ
isobutyraldehyde (**3a**)	95[a]	20.2
phenylacetaldehyde (**3b**)	91[a]	18.8
heptanal (**3c**)	98[a]	19.4
cyclohexanone (**3d**)	54	18.9

[a] (*E*) isomer only.

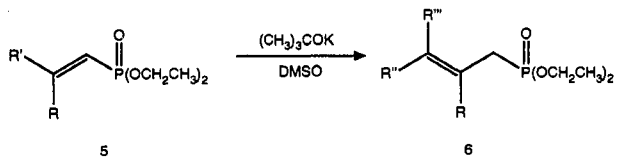
Table II. Conditions for Synthesis of Vinyl Phosphonates



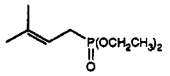
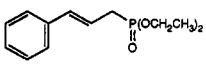
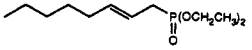
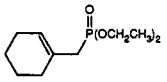
3a 5a

base	solvent	yield (%)
NaH	THF	95
$NaOCH_2CH_3$	THF	47
$(CH_3)_3COK$	THF	26
K_2CO_3	THF	38
K_2CO_3	DMSO	18

Table III. Isomerization of Vinyl Phosphonates to Allylic Phosphonates



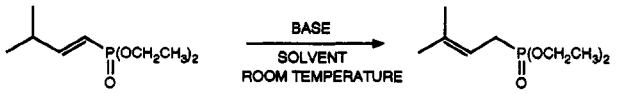
5 6

vinyl phosphonate	isomerization product	yield of allylic phosphonate 6 (%)	^{31}P NMR δ
5a		85	29.1
5b		92[a]	27.4 (*E*) 28.7 (*Z*)
5c		66[b]	28.5
5d		84	28.8

[a] 24:1 *E*/*Z* mixture. [b] *E* stereoisomer only.

In view of the tendency of allylic phosphonium salts to isomerize to the corresponding vinylphosphonium salts in the presence of base, it was surprising to find that vinyl phosphonates **5a-d** isomerized exclusively to the corresponding allylic phosphonates **6a-d**, when treated with a catalytic amount of potassium *tert*-butoxide in DMSO (Table III). The structural integrity of each isomerization product (**6a-d**) was verified by ^{31}P NMR analysis.

Table IV. Conditions for Isomerization of Allylic Phosphonates



5a 6a

base	solvent	yield (%)
$(CH_3)_3COK$	DMSO	85
$NaOCH_2CH_3$	DMSO	9
K_2CO_3	DMSO	0
K_2CO_3/18-crown-6	DMSO	0
K_2CO_3/18-crown-6	THF	0

The stereochemical outcome of the reactions listed in Tables I and III is also worth noting. All vinyl phosphonates prepared as outlined in Table I were shown to possess the (*E*)-configuration by ^1H NMR and ^{13}C NMR analysis.[19] In addition, ^{31}P NMR spectra for all vinyl phosphonates contained a single peak. The corresponding allylic phosphonates also proved to be of the (*E*)-configuration based on ^1H NMR coupling constants and ^{31}P NMR data. In only one of these isomerizations (**5b** → **6b**) was any (*Z*)-isomer detected in the reaction product. When **5b** was treated with a catalytic amount of $KOC(CH_3)_3$ at 20 °C for 5 h, ^1H NMR analysis indicated that the corresponding allylic phosphonate was a 24/1 mixture of *E*/*Z* stereoisomers.[20] However, when the reaction time was extended to 24 h no (*Z*)-isomer was observable by either ^1H or ^{31}P NMR analysis.

Table IV presents the results of a limited study to assess the conditions required for this isomerization. It is apparent from the yields in this study that the basicity of the *tert*-butoxide anion in DMSO[21] plays a crucial role in the isomerization of vinyl phosphonates to the corresponding allylic phosphonates in this investigation.

In conclusion, we have developed a novel and reliable synthesis of allylic phosphonates from the corresponding vinyl phosphonates. In addition to the facility with which each of these transformations occurs, the exclusive formation of (*E*)-stereoisomers points to the use of the allylic phosphonates (**6**) as versatile intermediates in the stereoselective synthesis of dienes and polyenes.

Experimental Section

General Methods. ^1H, ^{31}P, and proton-decoupled ^{13}C NMR spectra were recorded at 300, 121, and 75 MHz, respectively. ^1H and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$), and all chemical shifts are referenced to tetramethylsilane (TMS) as an internal standard. ^{13}C NMR data include a listing of coupling constants recorded for ^{31}P coupling to ^{13}C. ^{31}P NMR spectra were recorded in $CDCl_3$ using 85% phosphoric acid as an external standard. Analytical thin-layer chromatography (TLC) was conducted with aluminum-backed silica plates. Flash chromatography was performed on Kieselgel 60, 230–400 mesh. Aldehydes were distilled directly before use, and all other solvents were purified according to standard literature procedures. The spectral properties of all vinyl and allylic phosphonates were minimally consistent with ^1H NMR data reported in the literature.

(19) The stereochemical assignments were also confirmed by examining the $^3J_{C-P}$ coupling constants for each product. Such coupling constants have been shown to be stereodependent. See: Spassov, S. L.; Markova, L.; Mondeshka, D. M.; Tancheva, Ch. N.; Angelov, Ch. M. *Magn. Res. Chem.* **1985**, *23*, 578.

(20) The major diastereomer exhibited a ^1H NMR spectrum identical to that of the (*E*)-isomer reported in the literature.[24]

(21) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

When ^{13}C and ^{31}P NMR data were available for comparison, this was used as additional confirmation of the structure of products.

Synthesis of Vinyl Phosphonates 5. The ylide was generated under a nitrogen atmosphere by dropwise addition of 1.2 mmol of tetraethyl methylenediphosphonate (**4**)[14] in 2 mL of THF to a stirred solution of 1.1 mmol of sodium hydride in 2 mL of THF, maintained at a temperature of 15–20 °C by use of an external cold water bath. Subsequent addition of a solution of 1.0 mmol of aldehyde in 3 mL of THF was followed by stirring of this reaction mixture for an additional 0.5 h at room temperature. The mixture was then diluted with ether and extracted in successive order with 7:3 (v/v) 1 M aqueous NaOH/methyl alcohol (2 × 30 mL) to remove excess diphosphonate, 1:1 (v/v) H_2O/brine (1 × 30 mL), and brine (20 mL). The organic layer was dried over $MgSO_4$ and the solvent removed in vacuo to afford the vinyl phosphonates as colorless oils after evaporative (Kugelrohr) distillation.

Synthesis of Allylic Phosphonates 6. Vinyl phosphonate (1 equiv) and 0.25 equiv of potassium *tert*-butoxide were stirred in anhydrous dimethyl sulfoxide (2 mL per mmol of **5**) for 24 h. The mixture was subsequently diluted with ether and extracted with 10% aqueous NaCl (2 × 25 mL) and brine (20 mL). The organic layer was then dried over $MgSO_4$ and the solvent removed in vacuo to afford the allylic phosphonates. Flash chromatography to separate stereoisomers of **6b** on silica (diethyl ether) afforded the pure (*E*)- and (*Z*)-**6b**.

(*E*)-(3-Methyl-1-butenyl)phosphonic acid diethyl ester (5a): bp 141 °C (bath temperature, 0.25 mmHg); R_f = 0.73 (diethyl ether); ^1H NMR δ 6.79 [ddd, 1H, *J* = 16.0, 12.3, 6.0 Hz, H-C(2)], 5.61 [m, 1H, H-C(1)], 4.09 [m, 4H, POCH_2], 2.48 [m, 1H, H-C(3)], 1.35 [t, 6H, *J* = 7.0 Hz, $POCH_2CH_3$], 1.08 [d, 6H, *J* = 6.9 Hz, CH_3-C(3)]; ^{13}C NMR δ 159.7 [d, *J* = 4.0 Hz, C(2)], 113.0 [d, *J* = 188.0 Hz, C(1)], 61.6 [d, *J* = 5.6 Hz, POCH_2], 32.5 [d, *J* = 21.0 Hz, C(3)], 21.1 [CH_3-C(3)], 21.0 [CH_3-C(3)], 16.4 [d, *J* = 6.4 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 20.2. ^1H NMR data were consistent with that previously reported for this compound and confirmed the absence of the corresponding (*Z*)-stereoisomer, ^1H NMR data of which has also been published.[15]

(3-Methyl-2-butenyl)phosphonic acid diethyl ester (6a): bp 134 °C (bath temperature, 0.3 mmHg); R_f = 0.67 (diethyl ether); ^1H NMR δ 5.45 [m, 1H, H-C(2)], 4.06 [m, 4H, POCH_2], 2.53 [dd, 2H, *J* = 22.0, 7.2 Hz, H-C(1)], 1.74 [d, 3H, *J* = 5.7 Hz, CH_3-C(3)], 1.65 [d, 3H, *J* = 4.5 Hz, CH_3-C(3)], 1.29 [t, 6H, *J* = 7.0 Hz, $POCH_2CH_3$]; ^{13}C NMR δ 137.1 [d, *J* = 14.8 Hz, C(3)], 113.2 [d, *J* = 11.1 Hz, C(2)], 61.7 [d, *J* = 6.7 Hz, POCH_2], 26.4 [d, *J* = 140.0 Hz, C(1)], 25.7 [CH_3-C(3)], 17.9 [CH_3-C(3)], 16.4 [d, *J* = 6.0 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 29.1. ^1H, ^{13}C, and ^{31}P NMR data were consistent with those previously reported.[22]

(*E*)-(3-Phenyl-1-propenyl)phosphonic acid diethyl ester (5b): bp 206 °C (bath temperature, 0.3 mmHg); R_f = 0.74 (diethyl ether); ^1H NMR δ 7.37–7.20 [m, 5H, phenyl], 6.95 [m, 1H, H-C(2)], 5.66 [dd, 1H, *J* = 17.4, 1.8 Hz, H-C(1)], 4.10 [m, 4H, POCH_2], 3.58 [d, 2H, *J* = 6.3 Hz, H-C(3)], 1.35 [t, 6H, *J* = 7.2 Hz, $POCH_2CH_3$]; ^{13}C NMR δ 151.5 [d, *J* = 5.3 Hz, C(2)], 138.0, 137.2, 128.8, 128.6, 128.5, 126.6, 118.1 [d, *J* = 187.0 Hz, C(1)], 61.7 [d, *J* = 5.6 Hz, POCH_2], 40.4 [d, *J* = 23.0 Hz, C(3)], 16.4 [d, *J* = 6.3 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 18.8. ^1H NMR data were consistent with that previously reported.[23]

(*E*)-(3-Phenyl-2-propenyl)phosphonic acid diethyl ester (6b): bp 221 °C (bath temperature, 0.05 mmHg); R_f = 0.71 (diethyl ether); ^1H NMR δ 7.40–7.20 [m, 5H, phenyl], 6.55 [dd, 1H, *J* = 16.0, 5.3 Hz, H-C(3)], 6.18 [m, 1H, H-C(2)], 4.17 [m, 4H, POCH_2], 2.79 [ddd, 2H, *J* = 22.0, 7.5, 1.3 Hz, H-C(1)], 1.34 [t, 6H, *J* = 6.3 Hz, $POCH_2CH_3$]; ^{13}C NMR δ 136.7, 134.5 [d, *J* = 15.0 Hz, C(3)], 128.6, 128.5, 128.1, 127.5, 126.1, 118.7 [d, *J* = 12.0 Hz, C(2)], 62.2 [d, *J* = 6.6 Hz, POCH_2], 31.0 [d, *J* = 140.0 Hz, C(1)], 16.5 [d, *J* = 6.0 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 27.4. ^1H NMR data were consistent with that previously reported for the (*E*)-isomer.[24]

(*Z*)-(3-Phenyl-2-propenyl)phosphonic acid diethyl ester (6b): bp 219 °C (bath temperature, 0.1 mmHg); R_f = 0.68 (diethyl ether); ^1H NMR δ 7.31 [m, 5H, phenyl], 6.56 [dd, 1H, *J* = 13.4, 4.8 Hz, H-C(2)], 6.20 [m, 1H, H-C(3)], 4.15 [m, 4H, POCH_2], 3.88 [m, 1H, H-C(1)], 3.61 [m, 1H, H′-C(1)], 1.37 [t, 6H, *J* = 5.8 Hz, $POCH_2CH_3$]; ^{13}C NMR δ 132.7, 129.7 [d, *J* = 28.1 Hz, C(3)], 128.6, 128.5, 127.3, 126.2, 126.1, 104.1 [C(2)], 63.8 [POCH_2], 28.6 [d, *J* = 202.2 Hz, C(1)], 16.5 [d, *J* = 6.0 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 28.7. ^1H NMR data were consistent with that previously reported.[25]

(*E*)-1-Octenylphosphonic acid diethyl ester (5c): bp 171 °C (bath temperature, 0.4 mmHg); R_f = 0.79 (diethyl ether); ^1H NMR δ 6.80 [ddd, 1H, *J* = 17.1, 11.0, 5.0 Hz, H-C(2)], 5.65 [dd, 1H, *J* = 18.7, 4.1 Hz, H-C(1)], 4.08 [m, 4H, POCH_2], 2.22 [m, 2H, H-C(3)], 1.45 [m, 2H], 1.34 [t, 6H, *J* = 7.1 Hz, $POCH_2CH_3$], 1.31 [m, 6H], 0.90 [t, 3H, *J* = 7.0 Hz, H-C(8)]; ^{13}C NMR δ 153.8 [d, *J* = 4.4 Hz, C(2)], 116.6 [d, *J* = 187.4 Hz, C(1)], 61.5 [d, *J* = 5.5 Hz, POCH_2], 34.2 [d, *J* = 22.0 Hz, C(3)], 31.3, 27.5, 27.4, 22.4, 16.4 [d, *J* = 6.4 Hz, $POCH_2CH_3$], 14.0 [C(8)]; ^{31}P NMR δ 19.4. ^1H NMR data were consistent with that previously reported.[26]

(*E*)-2-Octenylphosphonic acid diethyl ester (6c): bp 163 °C (bath temperature, 0.3 mmHg); R_f = 0.69 (diethyl ether); ^1H NMR δ 5.59 [m, 1H, vinyl-H], 5.41 [m, 1H, vinyl-H], 4.10 [m, 4H, POCH_2], 2.54 [ddd, 2H, *J* = 19.5, 6.8, 4.8 Hz, H-C(1)], 2.04 [m, 2H], 1.32 [m, 6H], 1.31 [t, 6H, *J* = 7.1 Hz, $POCH_2CH_3$], 0.90 [t, 3H, *J* = 7.0 Hz, H-C(8)]; ^{13}C NMR δ 136.1 [d, *J* = 17.0 Hz, C(3)], 118.5 [d, *J* = 13.4 Hz, C(2)], 61.9 [d, *J* = 6.7 Hz, POCH_2], 34.7, 30.6 [d, *J* = 146.0 Hz, C(1)], 27.5, 27.4, 22.2, 16.4 [d, *J* = 6.5 Hz, $POCH_2CH_3$], 13.7 [C(8)]; ^{31}P NMR δ 28.5. ^1H NMR data were consistent with that previously reported.[27]

(Cyclohexylidenemethyl)phosphonic acid diethyl ester (5d): bp 169 °C (bath temperature, 0.5 mmHg); R_f = 0.63 (diethyl ether); ^1H NMR δ 5.36 [d, 1H, *J* = 21.0 Hz, C*H*P], 4.10 [m, 4H, POCH_2], 2.65 [m, 2H], 2.27 [m, 2H], 1.71 [m, 6H], 1.35 [t, 3H, *J* = 7.0 Hz, $POCH_2CH_3$]; ^{13}C NMR δ 167.8 [d, *J* = 3.0 Hz], 109.2 [d, *J* = 152.0 Hz, C(1)], 61.3 [d, *J* = 6.9 Hz, POCH_2], 39.1 [d, *J* = 24.0 Hz], 32.2 [d, *J* = 17.6 Hz], 28.7, 28.0, 25.9, 16.4 [d, *J* = 6.2 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 18.9; HRMS calcd for $C_{11}H_{21}O_3P$ 232.1228, found 232,1228. ^1H NMR data were consistent with that previously reported.[28]

[(1-Cyclohexenyl)methyl]phosphonic acid diethyl ester (6d): bp 174 °C (bath temperature, 0.3 mmHg); R_f = 0.81 (diethyl ether); ^1H NMR δ 5.61 [m, 1H, vinyl-H], 4.10 [m, 4H, POCH_2], 2.50 [d, 2H, *J* = 24.0 Hz, CH_2P], 2.11 [m, 4H], 1.58 [m, 4H], 1.31 [t, 6H, *J* = 7.6 Hz, $POCH_2CH_3$]; ^{13}C NMR δ 135.0 [d, *J* = 13.0 Hz], 126.5 [d, *J* = 10.7 Hz], 61.8 [d, *J* = 6.6 Hz, POCH_2], 39.1, 32.1 [d, *J* = 162.0 Hz, C(1)], 29.5, 22.9, 22.0, 16.5 [d, *J* = 6.1 Hz, $POCH_2CH_3$]; ^{31}P NMR δ 28.8; HRMS calcd for $C_{11}H_{21}O_3P$ 232.1228, found 232.1224. ^1H NMR and ^{31}P NMR data were consistent with that previously reported.[15,28]

(22) Hafner, A.; Philipsborn, W.; Salzer, A. *Helv. Chim. Acta* **1986**, *69*, 1757.

(23) Koizumi, T.; Tanaka, N.; Iwata, M.; Yoshii, E. *Synthesis* **1982**, 917.

(24) Drew, J.; Letellier, M.; Morand, P. Szabo, A. G. *J. Org. Chem.* **1987**, *52*, 4047.

(25) Hirao, T.; Hagihara, M.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3104.

(26) Hirao, T.; Ohshiro, Y.; Kerokawa, K.; Agawa, T. *Yukagaku* **1983**, *32*, 274.

(27) Canevet, C.; Roder, T.; Vostrowsky, O.; Bestmann, H. *Chem. Ber.* **1980**, *113*, 1115.

(28) Gerber, J. P.; Modro, T. A.; Wagener, C. C. P.; Zwierzak, A. *Heteroatom Chem.* **1991**, *2*, 643.