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Addition of Phosphorus-Stabilized Carbanions to Cyclic Enones and Further Transformations of the Reaction Products

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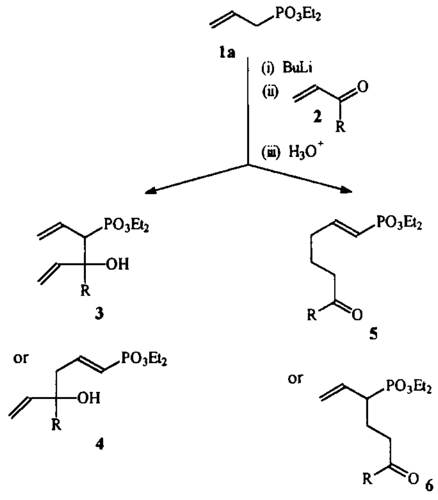
ABSTRACT

a-Lithiated diethyl alkylphosphonates react with cyclic enones according to a 1,2-addition, yielding the corresponding allylic alcohols (β-hydroxyalkylphosphonates). The alcohols undergo acid-catalyzed dehydration with preferential exocyclic location of the new olefinic bond; in some cases, allylic rearrangement to a 2° alcohol was observed. In pure methanol, allylic rearrangement is accompanied by the formation of an allyl methyl ether. Lithiated prop-2-enylphosphonate adds to the β-carbon (1,4-addition) via its γ-carbon; the only exception is 3-methylcyclohexenone, in which the methyl group directs the nucleophile toward the carbonyl center. © 1996 John Wiley & Sons, Inc.



SCHEME 1

INTRODUCTION

In most general terms, the addition of phosphorus-stabilized carbanions derived from allylic phosphonates (1a, "delocalized" carbanions) to the a,β-unsaturated carbonyl substrates (2) can lead to four types of products depending on the chemoselectivity of both reagents (Scheme 1). The reaction is attracting considerable attention because of its synthetic potential, and literature reports show that the reaction course depends on the structures of both substrates and on the reaction conditions. The reactions involving "localized" carbanions (a-lithiated alkylphosphonates) usually yield the 1,2-adducts as exclusive products [1,2], although both directions (1,2 or 1,4) can be achieved by changing the reaction conditions [3]. The latter result was explained by Seyden-Penne and coworkers as a consequence of the kinetic vs. thermodynamic control of the reaction [4]; the French authors later developed a theory of the factors controlling the regioselectivity of the addition, according to which "C$_4$ attack increases with

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Dedicated to Prof. Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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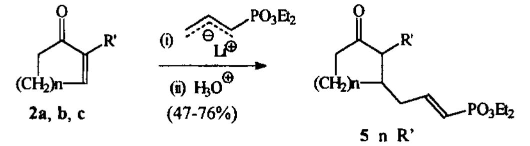
delocalization of the reagent's negative charge . . ." [5]. This conclusion was confirmed in the addition of allylic phosphonoamidates to cyclic enones (1,4-addition via the γ-carbon of the amide) [6], but, in the reaction with α,β-unsaturated aldehydes, only the 1,2-addition (via the γ-carbon of the carbanion) was reported [7].

In continuation of our work on the regioselectivity (α- vs. γ-carbons) in the reaction of the lithiated allylic phosphonates with electrophiles [8], and on the reaction of the phosphorus-stabilized carbanions with cyclic enones [9], we report now the reactions of "localized" and "delocalized" phosphonate carbanions with cyclic enones and some further transformations of the reaction products.

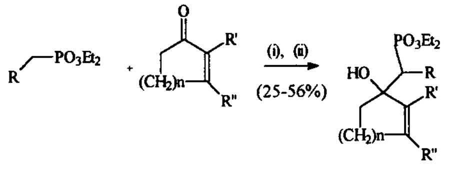
RESULTS AND DISCUSSION

Confirming earlier reports [1,2], lithiated diethyl methylphosphonate (**1b**) and diethyl ethylphosphonate (**1c**) reacted with cyclohexenone and cyclopentenone derivatives (**2**) exclusively at the carbonyl function, yielding (after protonation) tertiary alcohols **3** (Scheme 2). The alcohols can undergo dehydration upon heating, but they could be isolated in pure state (albeit in moderate yields) by column chromatography and stored at room temperature for reasonable periods of time. The reaction of the "delocalized" carbanion (derived from **1a**) with the same enones **2** was found to be substrate dependent. In the presence of a Cu(I) salt [10], enones **2a–c** reacted exclusively according to the 1,4-addition pattern via the γ-carbon atom of the nucleophile (Scheme 3). The course of the reaction is analogous to that reported for the addition of optically active allylic phosphonoamidates [6], when it was reported that, only when the steric bulk of the phosphonamide group was increased, was some of the 1,2-addition also observed. On the other hand, we have found that the substitution of the β-hydrogen in **2b** for the methyl group (**2d**) changes completely the regioselectivity with respect to both reagents, and the 1,2-adduct by the α-carbon of **1a** is the exclusive reaction product (Scheme 4). In our previous work [9, 11], when cyclohexenone substituted at the β-carbon with a potential leaving group was treated with the same lithiated allylic phosphonate, the reaction took place exclusively at the carbon β, and, following the addition-elimination mechanism, yielded the new 3-substituted cyclohexenone (Scheme 5). The difference in the outcome of the reactions given in Schemes 4 and 5 result most likely from the fact that in the latter the initial adduct of the carbanion to the β-carbon can be immediately stabilized by the expulsion of the leaving group (X^-) (the reaction approaching perhaps a single-step process, recognized as a mechanistic possibility for the nucleophilic vinylic substitution [12]). In the former reaction (Scheme 4), the initial (kinetic [4]) γ-adduct can be stabilized as such only in the independent quenching step. Instead, under the reaction conditions, it can undergo the retro-condensation reaction and form the thermodynamically more favored adduct to the



5	n	R'
a	1	Me
b	2	H
c	2	Me

SCHEME 3



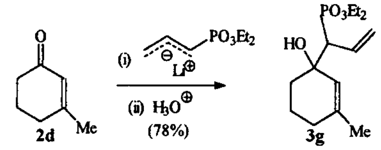
1b, R = H
1c, R = Me

2	n	R'	R''
a	1	Me	H
b	2	H	H
c	2	Me	H
d	2	H	Me

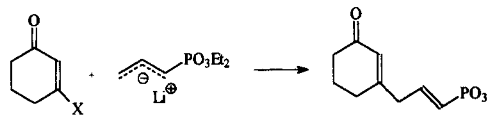
3	n	R	R'	R''
a	1	H	Me	H
b	2	H	H	H
c	2	Me	H	H
d	2	H	Me	H
e	2	H	H	Me
f	2	Me	H	Me

(i) BuLi, THF, -78°C
(ii) H_2O, NH_4Cl

SCHEME 2



SCHEME 4



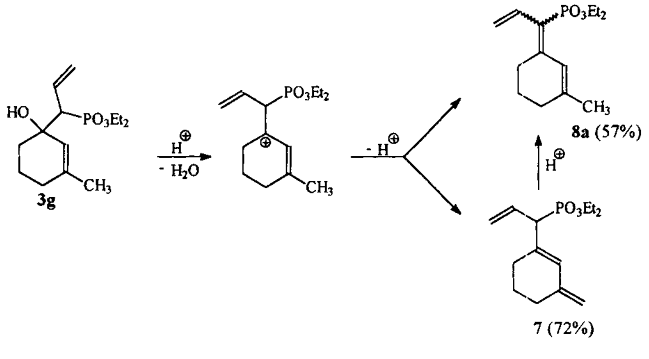
(X = Cl or OMe)

SCHEME 5

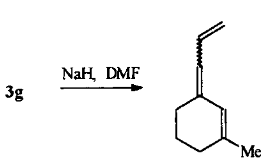
carbonyl group. Opposite regioselectivity observed for the reactions of **1a** with **2b** and **2d** suggests that the rate of the 4-retro-addition step for the latter is significantly greater than that for the former, possibly because a more stable (more substituted) alkene function is recovered in the case of the **2d** substrate.

The next part of this work is concerned with some aspects of the chemistry of alcohols **3**. As 2-hydroxyalkylphosphonates, they represent substrates for the Wadsworth–Emmons reaction as precursors for conjugated dienes. This can be illustrated by the conversion of **3g** into 1-methyl-3-(prop-2-enylidene)cyclohexene (Scheme 6), but the application of adducts **3** will be reported in a forthcoming publication. We have also been interested in the acid-catalyzed dehydration of alcohols **3**, since the reaction should lead to new alkenylphosphonic systems of further synthetic potential. When **3g** was incubated at room temperature in a benzene solution in the presence of the catalytic amount of *p*-toluenesulfonic acid (T*s*OH), it was smoothly converted into product **7**, still retaining the structure of an allylic phosphonate. When the reaction was carried out under reflux, or when the benzene solution of **7** was heated under reflux in the presence of TsOH, the triene **8a** (as an approximately 1:1 mixture of two stereoisomers) was found as the exclusive product. It is obvious that **7** represents the product of the kinetic control, reflecting faster deprotonation of the sterically more accessible 3-methyl group, while the formation of the fully conjugated triene system **8a** is responsible for the thermodynamic control (Scheme 7). The configuration of trienes **8a** was determined from the values of the $^3J_{CP}$ constant for the olefinic C-2 ^{13}C NMR signal ("small" *Z*, "large" *E*) of both isomers.

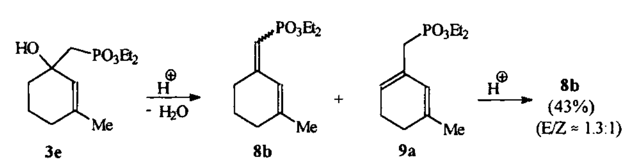
Dehydration of **3e** gave no evidence for the deprotonation of the 3-methyl group that should lead to the phosphonomethyl analog of **7**. At room temperature, the mixture of the exocyclic (**8b**) and the endocyclic (**9a**) dienes was formed; upon heating the solution under reflux, the mixture was converted completely to the **8b** isomer (*E*/*Z* ≈ 1.3:1; assignment as for **8a**) (Scheme 8). The product of the endocyclic dehydration **9a** (minor) was not isolated and fully identified, but its presence was clearly demonstrated in the ^{31}P NMR spectrum of the crude reaction product. While both stereoisomers of **8b** give rise to signals typical for the vinylphosphonates (δ_P 20.5, 19.3), the signal for **9b** (δ_P 27.5) corresponds well to the range typical for the allylphosphonate esters. The formation of the vinylic phosphonate **8b** as the final product provides information about the effect of the phosphoryl function on an adjacent olefinic bond. Methylenecyclohexane is thermodynamically less stable than 1-methylcyclohexene by ca. 3 kcal mol^{-1} (25°C) [13]; for the corresponding pair of dienes (1-methylene-2-cyclohexene vs. 1-methyl-2,6-cyclohexadiene), combustion measurements showed that the endocylic isomer is more stable by as much as 11 kcal mol^{-1} [14]. The fact that **8b** is preferred over **9a** gives clear evidence for a considerable stabilizing effect of the PO_3Et_2 functional group when attached to a terminal carbon of a conjugated diene system. It is, however, interesting to note that this conclusion may not be equally valid for the monoene systems; we have demonstrated earlier that under the conditions of prototropic equilibrium, diethyl 1-cyclohexenylmethylphosphonate represents 100% of the equilibrium mixture, with no exocyclic isomer, phosphonomethylene-cyclohexane detected [15]. The effect of the PO_3Et_2 group in the dehydration of alcohols **3** was confirmed in the reaction of **3d**, which, after its benzene solution had been heated with TsOH under reflux, yielded exclusively the exocyclic diene **8c** (Scheme 9). In this case, obviously because of the steric hindrance introduced by the 2-methyl



SCHEME 7



SCHEME 6



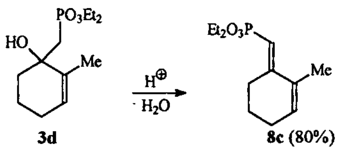
SCHEME 8

group, the product was formed as a single stereoisomer (E, $^{3}J_{C\text{-}2/P}$ = 23.9 Hz).

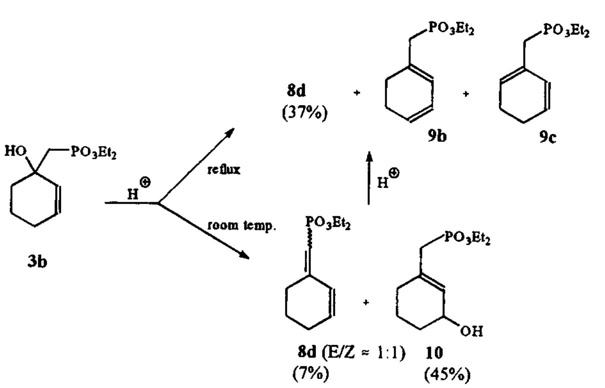
Dehydration of the alcohol **3b** took a slightly different course. At room temperature, some of the diene **8d** was formed, but the major product was the rearranged allylic alcohol **10**. Upon reflux, a complete dehydration was achieved, and a mixture of the exocyclic (**8d**, major) and two endocyclic dienes (**9b**, **9c**, minor, not isolated but identified from the ^{31}P NMR spectrum of the crude product) was obtained (Scheme 10).

The synthetic potential of the acid-catalyzed rearrangement of tertiary allylic alcohols of the cyclohex-1-en-3-ol system to the secondary isomers was recognized by Corey and Crouse almost 30 years ago [16]. Acidic treatment of 3-methyl-3-hydroxy-5-phenyl-pent-1-ene gave, on the other hand, only the dehydration products (isomeric dienes) with no rearranged (primary) alcohol [17]. In the field of hydroxyalkenylphosphonic systems, acid-catalyzed rearrangements of α-hydroxyallylic phosphonates to γ-hydroxyvinylic products (trapped as acetate derivatives) were utilized synthetically by Öhler and Zbiral [18]. In a detailed study of the stereochemical control in the allylic rearrangement of alcohols containing the diphenylphosphinoyl group in the β-position, Warren and coworkers noticed that elimination (dehydration) can interfere with the rearrangement [19]. For the 2-benzylidenecyclohexanone derivatives, the authors observed exclusive elimination products (the olefinic bond not moving away from the phenyl group). 2-Benzylidene-1-(diphenylphosphinoylmethyl)cyclohexanol yielded, however, only (E,E)-6-benzylidene-1-(diphenylphosphinoylmethyl)cyclohexene, i.e., the product of the endocyclic dehydration, without any isomer with the exocyclic location of the new olefinic bond, available for the conjugation with the $Ph_2P(O)$ substituent, being formed. We consider, therefore, the observed exclusive or preferential formation of the exocyclic dienes **8b–d** (Schemes 8–10) to be rather unexpected, and possible reasons for that regioselectivity are being currently investigated. Secondary alcohol **10** was isolated in a pure state and could be used as the substrate in further reactions. For example, it was oxidized to the corresponding cyclohexenone derivative **11**, the same product that was obtained from the addition-elimination reaction between the lithiated diethyl methylphosphonate and 3-methoxycyclohexenone [9]. Preparation of **11** via both routes is shown in Scheme 11—it has to be noted that the relative position of the C-1 and C-3 carbons in the cyclohexenone skeleton is retained in one route and reversed in the other.

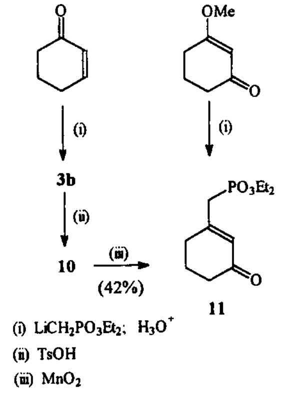
Allylic rearrangement, free of any elimination, was, however, observed when the alcohol **3b** was heated under reflux in pure methanol, yielding 100% of the corresponding allyl ether **12** (Scheme 12). Formation of the rearranged allylic ethers from allylic alcohols and alkanols was reported as early as in 1945 [20], but, in those cases, the reaction was car-



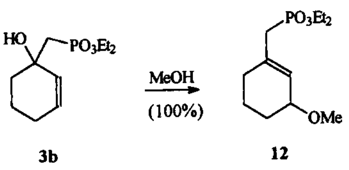
SCHEME 9



SCHEME 10



SCHEME 11



SCHEME 12

ried out in the presence of strong acid, and the rearrangement was driven by the formation of a conjugated system of π bonds. It seems that the driving force for the observed **3b** → **12** rearrangement can be the higher degree of substitution of the olefinic bond in the latter. Since we have found that even prolonged refluxing of **3e**, as opposed to **3b**, in MeOH gave no reaction and allowed us to recover the unchanged substrate, it seems that steric accessibility of the 3° vs. 2° carbons in the intermediate carbocations derived from **3e** and **3b** by the solvent is important for the rearrangement to occur. The lack of reaction of **3e** can also be attributed to a reluctance of the substituted sp^2 carbon-3 of **3e** to be converted to an sp^3 center.

EXPERIMENTAL SECTION

Solvents and commercially available substrates were purified by conventional methods immediately before use. Reactions involving lithiated reagents were carried out in an atmosphere of dry nitrogen. For column chromatography, Merck Kieselgel 60 (0.063–0.200 mm) was used as a stationary phase. Mass spectra were recorded on a Varian MAT-212 double-focusing direct-inlet spectrometer at an ionization potential of 70 eV. IR spectra were recorded on a Bomen, Inc., Michelson 100 spectrometer as solutions in $CHCl_3$. NMR spectra were recorded on a Bruker AC 300 spectrometer for solutions in $CDCl_3$ (Uvasol, Merck). The chemical-shift values are given in δ relative to the solvent (^{1}H: 7.24 ppm; ^{13}C: 77.0 ppm). ^{31}P NMR chemical-shift values are given relative to 85% H_3PO_4 as an external standard. Heteronuclear proton-carbon correlation spectra as well as NOE experiments were performed when necessary to assign structures unambiguously. Elemental analyses (C, N, H) were carried out at the Chemistry Department, University of Cape Town.

Preparation of Diethyl (1-Hydroxycyclohex-2-enyl)alkylphosphonates 3a–3f

General Procedure. *n*-Butyllithium (1.1 mol equiv.) (1.6 mol dm^{-3} solution in hexane) was diluted with THF (ca. 3 mL/mmol of phosphonate). To this solution, cooled at −78°C, was added dropwise with stirring a solution of alkylphosphonic acid diethyl ester (**1b** and **1c**; 1.0 mol equiv.) dissolved in THF (ca. 1 mL/mmol of phosphonate), and the solution was stirred at that temperature for 60 minutes. The electrophile **2** (1,2 mol equiv.) was dissolved in THF (ca. 1 mL/mmol of phosphonate) and then added to the reaction mixture and stirred at −78°C for 2 hours. Saturated aqueous NH_4Cl was added, and the solution was allowed to warm to room temperature. The mixture was then extracted with ether (3 × 20 mL). The combined ether layers were dried ($MgSO_4$/Na_2SO_4) and filtered, and the solvent was removed under reduced pressure. The products were purified by column chromatography using ethyl acetate as eluent to give the following compounds.

Diethyl(1-hydroxy-2-methylcyclopent-2-enyl) methylphosphonate **3a** *(0.65 g, 39,1%).* ^{1}H NMR δ 1.31 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^a); 1.32 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^b); 1.68 (3H; d; J_{HH} 1.7 Hz; CH_3 on C(2)); 1.85 (1H; d of d; J_{HP} 18.7 Hz; J_{HH} 15.1 Hz; α-CH); 2.02 (1H; m; CH on C(5)); 2.22 (1H; d of d; J_{HP} 16.7 Hz; J_{HH} 15.3 Hz; α-CH); 2.18–2.34 (3H; m; CH_2 on C(4), CH on C(5)); 3.89 (1H; s; OH); 4.08 (2H; quint; J_{HP} 7.1 Hz; J_{HH} 7.1 Hz; CH_2 of POEt^a); 4.10 (2H; quint; J_{HP} 7.1 Hz; J_{HH} 7.1 Hz; CH_2 of POEt^b); 5.47 (1H; s; CH on C(3)); ^{31}P NMR δ 30.71; ^{13}C NMR δ 10.83 (q; J_{CH} 123.6 Hz; CH_3 on C(2)); 15.74 (q; J_{CH} 125.6 Hz; CH_3 of POEt^a); 15.82 (q; J_{CH} 125.6 Hz; CH_3 of POEt^b); 28.33 (t; J_{CH} 129.3 Hz; CH_2 on C(4)); 33.94 (d of t; J_{CP} 136.0 Hz; J_{CH} 126.1 Hz; α-CH_2); 37.93 (t; J_{CH} 130.7 Hz; CH_2 C(5)); 61.09 (t; J_{CH} 147.6 Hz; CH_2 of POEt^a); 61.84 (t; J_{CH} 147.6 Hz; CH_2 of POEt^b); 81.80 (d; J_{CP} 4.1 Hz; C of C(1)); 126.96 (d; J_{CH} 160.4 Hz; CH on C (3)); 142.64 (d; J_{CP} 14.0 Hz; C of C(2)); MS *m/z* 230 (($M^+ - H_2O$) 33%), 93 ($C_7H_9^+$ 56%), 92 ($C_7H_8^+$ 100%), 79 (PO_3^+ 7%), 29 ($C_2H_5^+$ 9%), 15 (CH_3^+ 1%); IR ν/cm^{-1} 3019 (s; OH), 1221 (s; P=O); anal. calcd for $C_{11}H_{21}PO_4$ (248,26): C, 53.22; H, 8.53. Found: C, 52.66; H, 9.21.

Diethyl(1-hydroxycyclohex-2-enyl)methylphosphonate **3b** *(1.78 g, 54.3%).* ^{1}H NMR δ 1.27 (3H; t; J_{HH} 7.1 Hz; CH_3 of POEt^a); 1.28 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^b); 1.51–1.57 (2H; m; CH_2 on C(5)); 1.70–1.78 (2H; m; CH_2 on C(6)); 1.83–2.12 (4H; m; CH_2 on C(4), α-CH_2); 3.91 (1H; s; OH); 4.05 (4H; m; 2 × CH_2 of POEt); 5.70 (2H; m; CH on C(2), CH on C(3)); ^{31}P NMR δ 29.98; ^{13}C NMR δ 16.22 (q; J_{CH} 129.0 Hz; CH_3 of POEt^a); 16.30 (q; J_{CH} 129.0 Hz; CH_3 of POEt^b); 18.92 (t; J_{CH} 127.8 Hz; CH_2 on C(5)); 24.72 (t; J_{CH} 125.5 Hz; CH_2 on C(4)); 36.93 (d of t; J_{CP} 14.6 Hz; J_{CH} 130.4 Hz; CH_2 on C(6)); 37.88 (d of t; J_{CP} 139.7 Hz; J_{CH} 130.7 Hz; α-CH_2); 61.51 (t; J_{CH} 148.9 Hz; CH_2 of POEt^a); 61.70 (t; J_{CH} 148.9 Hz; CH_2 of POEt^b); 67.68 (d; J_{CP} 4.3 Hz; C of C(1)); 129.35 (d; J_{CH} 155.2 Hz; CH on C(3)); 131.98 (d of d; J_{CP} 11.8 Hz; J_{CH} 161.9 Hz; CH on C(2)); MS *m/z* 249 (($M + 1)^+ < 1\%$), 248 (M^+ 1%), 229 ($C_{11}H_{18}PO_3^+$ 92%), 93 ($C_7H_9^+$ 46%), 92 ($C_7H_8^+$ 65%), 91 ($C_7H_7^+$ 100%), 79 (PO_3^+ 20%), 29 ($C_2H_5^+$ 56%), 15 (CH_3^+ 7%); IR ν/cm^{1} 3436 (s; OH), 1230 (s; P=O); anal. calcd for $C_{11}H_{21}PO_4$ (248,26): C, 53.22; H, 8.53. Found: C, 52.55; H, 8.82.

Diethyl 1-(1-Hydroxycyclohex-2-enyl)ethylphosphonate **3c** (*1.76 g, 55.7%*) (*Isomer A*). ^{1}H NMR δ 1.05 (3H; d of d; J_{HP} 17.4 Hz; J_{HH} 7.3 Hz; β-CH$_3$); 1.28 (3H; t; J_{HH} 7.1 Hz; CH$_3$ of POEt^a); 1.29 (3H; t; J_{HH} 7.1 Hz; CH$_3$ of POEt^b); 1.55–1.65 (2H; m; CH$_2$ on C(5)); 1.77–1.83 (2H; m; CH$_2$ on C(6)); 1.93–2.10 (3H; m; CH$_2$ on C(4), α-CH); 4.09 (4H; m; 2 × CH$_2$ of POEt); 4.36 (1H; s; OH); 5.42 (1H; d; J_{H2H3} 9.7 Hz; CH on C(2)); 5.88 (1H; d of d; J_{H3H2} 9.7 Hz; J_{H3H4} 5.6 Hz; CH on C(3)); ^{31}P NMR δ 33.66; ^{13}C NMR δ 11.01 (d of q; J_{CP} 4.9 Hz; J_{CH} 129.2 Hz; β-CH$_3$); 16.29 (q; J_{CH} 126.7 Hz; CH$_3$ of POEt^a); 16.37 (q; J_{CH} 126.7 Hz; CH$_3$ of POEt^b); 18.12 (t; J_{CH} 129.8 Hz; CH$_2$ on C(5)); 24.71 (t; J_{CH} 126.6 Hz; CH$_2$ on C(4)); 31.65 (d of t; J_{CP} 3.0 Hz; J_{CH} 127.5 Hz; CH$_2$ on C(6)); 41.80 (d of d; J_{CP} 133.7 Hz; J_{CH} 129.3 Hz; α-CH); 61.52 (t; J_{CH} 147.6 Hz; CH$_2$ of POEt^a); 61.85 (t; J_{CH} 147.6 Hz; CH$_2$ of POEt^b); 70.52 (s; C of C(1)); 131.10 (d; J_{CH} 156.0 Hz; CH on C(3)); 131.43 (d of d; J_{CP} 14.2 Hz; J_{CH} 156.0 Hz; CH on C(2)); (Isomer B) ^{1}H NMR δ 1.13 (3H; d of d; J_{HP} 18.0 Hz; J_{HH} 7.5 Hz; β-CH$_3$); 1.28 (3H; t; J_{HH} 7.0 Hz; CH$_3$ of POEt^a); 1.29 (3H; t; J_{HH} 7.0 Hz; CH$_3$ of POEt^b); 1.59–1.71 (2H; m; CH$_2$ on C(5)); 1.79–1.91 (2H; m; CH$_2$ on C(6)); 1.97–2.11 (3H; m; CH$_2$ on C(4), α-CH); 4.08 (4H; m; 2 × CH$_2$ of POEt); 4.39 (1H; s; OH); 5.80 (2H; m; CH on C(2), CH on C(3)); ^{31}P NMR δ 33.56; ^{13}C NMR δ 10.52 (d of q; J_{CP} 4.7 Hz; J_{CH} 129.2 Hz; β-CH$_3$); 16.28 (q; J_{CH} 126.7 Hz; CH$_3$ of POEt^a); 16.36 (q; J_{CH} 126.7 Hz; CH$_3$ of POEt^b); 18.67 (t; J_{CH} 129.8 Hz; CH$_2$ on C(5)); 24.84 (t; J_{CH} 126.6 Hz; CH$_2$ on C(4)); 34.77 (d of t; J_{CP} 10.0 Hz; J_{CH} 127.5 Hz; CH$_2$ on C(6)); 41.43 (d of d; J_{CP} 133.3 Hz; J_{CH} 129.3 Hz; α-CH); 61.57 (t; J_{CH} 147.6 Hz; CH$_2$ of POEt^a); 61.76 (t; J_{CH} 147.6 Hz; CH$_2$ of POEt^b); 70.25 (s; C of C(1)); 129.87 (d of d; J_{CP} 13.1 Hz; J_{CH} 156.0 Hz; CH on C(2)); 130.96 (d; J_{CH} 156.0 Hz; CH on C(3)); MS *m/z* 245 ($C_{12}H_{22}PO_3^+$ 8%), 244 ($C_{12}H_{21}PO_3^+$ 20%), 243 ($C_{12}H_{20}PO_3^+$ 68%), 106 ($C_8H_{10}^+$ 67%), 105 ($C_8H_9^+$ 100%), 91 ($C_7H_7^+$ 75%), 79 (PO_3^+ 30%), 29 ($C_2H_5^+$ 29%), 15 (CH_3^+ 2%); IR υ/cm^{-1} 3419 (s; OH), 1219 (s; P=O); anal. calcd for $C_{12}H_{23}PO_4$ (262.28): C, 54.95; H, 8.84. Found: C, 54.74; H, 9.02.

Diethyl(1-Hydroxy-2-methylcyclohex-2-enyl) methylphosphonate **3d** (*0.49 g, 28.5%*). ^{1}H NMR δ 1.27 (6H; t; 7.0 Hz; 2 × CH$_3$ of POEt); 1.32–1.70 (3H; m; CH$_2$ on C(5), CH on C(6)); 1.68 (3H; d; J_{HP} 1.6 Hz; CH$_3$ on C(2)); 1.80–2.00 (3H; m; CH$_2$ on C(4), CH on C(6)); 1.92 (1H; d of d; J_{HP} 18.5 Hz; J_{HH} 15.4 Hz; α-CH); 2.24 (1H; d of d; J_{HP} 17.4 Hz; J_{HH} 15.5 Hz; α-CH); 3.75 (1H; s; OH); 4.07 (4H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH$_2$ of POEt); 5.42 (1H; s; CH on C(3)); ^{31}P NMR δ 30.60; ^{13}C NMR δ 15.99 (q; J_{CH} 127.5 Hz; CH$_3$ of POEt^a); 16.06 (q; J_{CH} 127.5 Hz; CH$_3$ of POEt^b); 17.25 (q; J_{CH} 126.0 Hz; CH$_3$ on C(2)); 19.12 (t; J_{CH} 126.0 Hz; CH$_2$ on C(5)); 25.00 (t; J_{CH} 126.5 Hz; CH$_2$ on C(4)); 34.53 (d of t; J_{CP} 134.2 Hz; J_{CH} 130.0 Hz; α-CH$_2$); 36.71 (t; J_{CH} 126.3 Hz; CH$_2$ on C(6)); 61.18 (t; J_{CH} 147.6 Hz; CH$_2$ of POEt^a); 61.48 (t; J_{CH} 147.6 Hz; CH$_2$ of POEt^b); 71.03 (s; C of C(1)); 125.34 (d; J_{CH} 153.0 Hz; CH on C(3)); 136.63 (d; J_{CP} 15.8 Hz; C of C(2)); MS *m/z* 262 (M$^+$ < 1%), 243 ($C_{12}H_{20}PO_3^+$ 84%), 187 ($C_8H_{12}PO_3^+$ 77%), 105 ($C_8H_9^+$ 100%), 79(PO_3^+ 26%), 29 ($C_2HH_5^+$ 45%), 15 (CH_3^+ 5%); IR υ/cm^{-1} 3019 (s; OH), 1221 (s; P=O); anal. calcd for $C_{12}H_{23}PO_4$ (262.28): C, 54.95; H, 8.84. Found: C, 54.49; H, 9.54.

Diethyl(1-Hydroxy-3-methylcyclohex-2-enyl) methylphosphonate **3e** (*0.60 g, 1.5%*). ^{1}H NMR δ 1.29 (6H; t; J_{HH} 7.1 Hz; 2 × CH$_3$ of POEt); 1.54–1.74 (2H; m; CH$_2$ on C(5)); 1.63 (3H; s; CH$_3$ on C(3)); 1.75–1.92 (4H; m; CH$_2$ on C(4), CH$_2$ on C(6)); 2.01 (1H; d; J_{HP} 16.3 Hz; α-CH^a); 2.04 (1H; d; J_{HP} 16.3 Hz; α-CH^b); 3.82 (1H; s; OH); 4.05 (2H; quint; J_{HP} 7.0 Hz; J_{HH} 7.0 Hz; CH$_2$ of POEt^a); 4.08 (2H; quint; J_{HP} 7.0 Hz; J_{HH} 7.0 Hz; CH$_2$ of POEt^b); 5.43 (1H; s; CH on C(2)); ^{31}P NMR δ 30.18; ^{13}C NMR δ 15.81 (q; J_{CH} 127.2 Hz; CH$_3$ of POEt^a); 15.89 (q; J_{CH} 127.2 Hz; CH$_3$ of POEt^b); 18.80 (t; J_{CH} 128.4 Hz; CH$_2$ on C(5)); 23.07 (q; J_{CH} 126.3 Hz; CH$_3$ on C(3)); 29.34 (t; J_{CH} 125.5 Hz; CH$_2$ on C(4)); 36.12 (d of t; J_{CP} 8.6 Hz; J_{CH} 127.7 Hz; CH$_2$ on C(6)); 37.88 (d of t; J_{CP} 134.0 Hz; J_{CH} 130.0 Hz; α-CH$_2$); 61.04 (t; J_{CH} 147.4 Hz; 2 × CH$_2$ of POEt); 67.74 (s; C of C(1)); 126.46 (d of d; J_{CP} 12.2 Hz; J_{CH} 157.5 Hz; CH on C(2)); 136.65 (s; C of C(3)); MS *m/z* 244 ($C_{12}H_{21}PO_3^+$ 49%), 243 ($C_{12}H_{20}PO_3^+$ 84%), 187 ($C_8H_{12}PO_3^+$ 97%), 106 ($C_8H_{10}^+$ 62%), 105 ($C_8H_9^+$ 100%), 79 (PO_3^+ 21%), 29 ($C_2H_5^+$ 20%); IR υ/cm^{-1} 3436 (s; OH), 1231 (s; P=O); anal. calcd for $C_{12}H_{23}PO_4$ (262.28): C, 54.95; H, 8.84. Found: C, 54.61; H, 9.10.

Diethyl 1-(1-Hydroxy-3-methylcyclohex-2-enyl) ethylphosphonate **3f** *Isomer A* (*0.39 g, 24.9%*). ^{1}H NMR δ 1.04 (3H; d of d; J_{HP} 17.4 Hz; J_{HH} 7.6 Hz; β-CH$_3$); 1.29 (3H; t; J_{HH} 7.1 Hz; CH$_3$ of POEt^a); 1.30 (3H; t; J_{HH} 7.1 Hz; CH$_3$ of POEt^b); 1.57–1.64 (2H; m; CH$_2$ on C(5)); 1.66 (3H; s; CH$_3$ on C(3)); 1.73–1.86 (4H; m; CH$_2$ on C(4), CH$_2$ on C(6)); 2.06 (1H; d of q; J_{HP} 19.1 Hz; J_{HH} 7.4 Hz; α-CH); 4.09 (2H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH$_2$ of POEt^a); 4.10 (2H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH$_2$ of POEt^b); 4.32 (1H; s; OH); 5.16 (1H; s; CH on C(2)); ^{31}P NMR δ 33.93; ^{13}C NMR δ 10.72 (d of q; J_{CP} 5.0 Hz; J_{CH} 133.0 Hz; β-CH$_3$); 15.93 (q; J_{CH} 127.7 Hz; CH$_3$ of POEt^a); 16.00 (q; J_{CH} 127.7 Hz; CH$_3$ of POEt^b); 18.17 (t; J_{CH} 126.6 Hz; CH$_2$ on C(5)); 23.34 (q; J_{CH} 125.7 Hz; CH$_3$ on C(3)); 29.38 (t; J_{CH} 123.8 Hz; CH$_2$ on C(4)); 30.94 (d of t; J_{CP} 2.9 Hz; J_{CH} 123.1 Hz; CH$_2$ on C(6)); 41.73 (d of d; J_{CP} 133.4 Hz; J_{CH} 129.0 Hz; α-CH); 61.08 (t; J_{CH} 147.2 Hz; CH$_2$ of POEt^a); 61.38 (t; J_{CH} 147.2 Hz; CH$_2$ of POEt^b);

70.75 (s; C of C(1)); 125.60 (d of d; J_{CP} 17.8 Hz; J_{CH} 167.6 Hz; CH on C(2)); 138.86 (s; C of C(3)); Isomer B (0.25 g, 15.7%), ^{1}H NMR δ 1.13 (3H; d of d; J_{HP} 18.0 Hz; J_{HH} 7.3 Hz; β-CH_3); 1.29 (3H; t; J_{HH} 7.3 Hz; CH_3 of POEt^{a}); 1.31 (3H; t; J_{HH} 7.3 Hz; CH_3 of POEt^{b}); 1.58–1.70 (2H; m; CH_2 on C(5)); 1.65 (3H; s; CH_3 on C(3)); 1.70–1.85 (4H; m; CH_2 on C(4), CH_2 on C(6)); 2.05 (1H; d of q; J_{HP} 19.9 Hz; J_{HH} 7.5 Hz; α-CH); 4.08 (4H; m; 2 × CH_2 of POEt); 5.54 (1H; s; CH on C(2)); ^{31}P NMR δ 33.76; ^{13}C NMR δ 10.56 (d of q; J_{CP} 4.8 Hz; J_{CH} 129.3 Hz; β-CH_3); 16.32 (q; J_{CH} 131.4 Hz; CH_3 of POEt^{a}); 16.40 (q; J_{CH} 131.4 Hz; CH_3 of POEt^{b}); 19.03 (t; J_{CH} 132.9 Hz; CH_2 on C(5)); 23.92 (q; J_{CH} 126.0 Hz; CH_3 on C(3)); 29.88 (t; J_{CH} 123.4 Hz; CH_2 on C(4)); 34.45 (d of t; J_{CP} 9.8 Hz; J_{CH} 126.3 Hz; CH_2 on C(6)); 41.70 (d of d; J_{CP} 133.1 Hz; J_{CH} 130.6 Hz; α-CH); 61.49 (t; J_{CH} 149.8 Hz; CH_2 of POEt^{a}); 61.60 (t; J_{CH} 149.8 Hz; CH_2 of POEt^{b}); 70.91 (s; C of C(1)); 124.41 (d of d; J_{CP} 5.9 Hz; J_{CH} 156.8 Hz; CH on C(2)); 138.92 (s; C of C(3)); MS *m/z* 259 ($C_{13}H_{24}PO_3^+$ 17%), 258 ($C_{13}H_{23}PO_3^+$ 100%), 120 ($C_9H_{12}^+$ 86%), 105 ($C_8H_9^+$ 47%), 79 (PO_3^+ 16%), 29 ($C_2H_5^+$ 19%); IR υ/cm^{-1} 3426 (s; OH), 1219 (s; P=O); anal. calcd for $C_{13}H_{25}PO_4$ (276.31): C, 56.51; H, 9.12. Found: C, 56.40; H, 9.45.

Reaction of **1a** *with Enones* **2**. *General Procedure*

n-Butyllithium (1.1 mol equiv.) (1.6 mol dm^{-3} solution in hexane) was diluted with THF (ca. 3 mL per mmol of phosphonate). To this solution, cooled at −78°C, was added dropwise with stirring a solution of **1a** (1.0 mol equiv.) dissolved in THF (ca. 1 mL per mmol of phosphonate), and the solution was stirred at that temperature for 60 minutes. Copper (I) iodide (0.55 mol equiv.) was then added, and the solution was stirred at −78°C for an additional hour. The electrophile **2** (0.75 mol equiv.), dissolved in THF (ca. 1 mL per mmol of phosphonate), was then added, and the reaction mixture was stirred at −78°C for 60 minutes. Saturated aqueous NH_4Cl was added, and the solution was allowed to warm to room temperature. The solution was stirred until the green color present in the organic phase had disappeared. The mixture was then extracted with ether (3 × 20 mL). The combined ether layers were dried ($MgSO_4$/Na_2SO_4), filtered, and the solvent was removed under reduced pressure. The products were purified and identified as indicated for individual compounds.

Diethyl 3-(2-Methyl-3-oxocyclopentyl)prop-1-enylphosphonate **5a**. Colorless oil purified by bulb-to-bulb distillation (oven temp. 175°C/0.35 mmHg) (1.18 g, 76.3%), ^{1}H NMR δ 1.01 (3H; d; J_{HH} 5.2 Hz; CH_3 on C(2)); 1.25 (3H; t; J_{HH} 7.2 Hz; CH_3 of POEt^{a}); 1.26 (3H; t; J_{HH} 7.2 Hz; CH_3 of POEt^{b}); 1.38, 1.71, 1.42–2.19, 2.51 (1H, 2H, 4H, 1H, four m, CH_2 on C(5), CH_2 on C(4), CH on C(1), CH on C(2), γ-CH_2); 4.01 (4H; quint; J_{HP} 6.9 Hz; J_{HH} 7.2 Hz; 2 × CH_2 of POEt); 5.68 (1h; d of d; J_{HP} 23.2 Hz; J_{HH} 17.2; Hz; α-CH); 6.70 (1H; m; β-CH); ^{31}P NMR δ 18.30; ^{13}C NMR δ 11.96 (q; J_{CH} 127.5 Hz; CH_3 on C(2)); 15.73 (q; J_{CH} 127.0 Hz; CH_3 of POEt^{a}); 15.81 (q; J_{CH} 127.0 Hz; CH_3 of POEt^{b}); 26.32 (t; J_{CH} 130.8 Hz; CH_2 on C(5)); 36.42 (t; J_{CH} 130.8 Hz; CH_2 on C(4)); 38.17 (d of t; J_{CP} 22.2 Hz; J_{CH} 115.1 Hz; γ-CH_2); 2.99 (d; J_{CH} 128.2 Hz; CH on C(1)); 49.03 (d; J_{CH} 123.0 Hz; CH on C(2)); 60.97 (t; J_{CH} 147.1 Hz; CH_2 of POEt^{a}); 61.04 (t; J_{CH} 147.1 Hz; CH_2 of POEt^{b}); 118.69 (d of d; J_{CP} 186.9 Hz; J_{CH} 156.3 Hz; α-CH); 149.92 (d of d; J_{CP} 4.2 Hz; J_{CH} 155.8 Hz; β-CH); 218.80 (s; C of C(3)); MS *m/z* 275 ((M + 1)$^+$ 82%), 178 ($C_7H_{15}PO_3^+$ 100%), 138 ($C_9H_{14}O^+$ 39%), 122 ($C_8H_{10}O^+$ 88%), 111 ($C_7H_{11}O^+$ 28%), 79 (PO_3^+ 38%), 29 ($C_2H_5^+$ 66%), 15 (CH_3^+ 5%); IR ν/cm^{-1} 1667 (s; C=O), 1217 (s; P=O); Anal. calcd for $C_{13}H_{23}PO_4$ (274.29): C, 56.93; H, 8.45. Found: C, 56.64; H, 8.66.

Diethyl 3-(3-Oxocyclohexyl)prop-1-enylphosphonate **5b**. Colorless oil purified by column chromatography (EtOAc/$CHCl_3$, 1:5) (0.73 g, 47.1%), ^{1}H NMR δ 1.27 (3H; t; J_{HH} 8.8 Hz; CH_3 of POEt^{a}); 1.28 (3H; t; J_{HH} 8.8 Hz; CH_3 of POEt^{b}); 1.62 (1H; m; CH on C(5)); 1.64–2.05 (5H; m; CH_2 on C(6), CH on C(1), CH on C(5), CH on C(4)); 2.22 (2H; d of d; J_{H1H6} 5.6 Hz; J_{H1H2} 5.6 Hz; γ-CH_2); 2.35 (3H; m; CH_2 on C(2), CH on C(4)); 4.01 (2H; quint; J_{HP} 7.1 Hz; J_{HH} 7.1 Hz; CH_2 of POEt^{a}; 4.04 (2H; quint; J_{HP} 7.1 Hz; J_{HH} 7.1 Hz; CH_2 of POEt^{b}); 5.64 (1H; d of d of t; J_{HP} 20.7 Hz; $J_{H\alpha H\beta}$ 18.4 Hz; $J_{H\alpha H\gamma}$ 1.2 Hz; α-CH); 6.66 (1H; d of of d of t; J_{HP} 21.6 $J_{H\beta H\alpha}$ 17.0 Hz; $J_{H\beta H\gamma}$ 6.8 Hz; β-CH); ^{31}P NMR δ 18.31; ^{13}C NMR δ 15.66 (q; J_{CH} 126.1 Hz; CH_3 on POEt^{a}); 15.74 (q; J_{CH} 126.1 Hz; CH_3 on POEt^{b}); 24.26 (t;J_{CH} 127.3 Hz; CH_2 on C(5)); 30.15 (t; J_{CH} 125.0 Hz; CH_2 on C(6)); 37.31 (d; J_{CH} 128.7 Hz; CH on C(1)); 40.31 (d of t; J_{CP} 22.2 Hz; J_{CH} 126.5 Hz; γ-CH_2); 40.53 (t; J_{CH} 127.7 Hz; CH_2 on C(4)); 46.93 (t; J_{CH} 130.4 Hz; CH_2 on C(2)); 60.98 (t; J_{CH} 147.1 Hz; CH_2 of POEt^{a}); 61.05 (t; J_{CH} 147.1 Hz; CH_2 of POEt^{b}); 118.75 (d of d; J_{CH} 186.9 Hz; J_{CH} 156.3 Hz; α-CH); 149.68 (d of d; J_{CP} 8.5 Hz; J_{CH} 156.0 Hz; β-CH); 209.87 (s; C of C(3)); MS *m/z* 274 (M$^+$ 2%), 178 ($C_7H_{15}PO_3^+$ 100%), 150 ($C_5H_{11}PO_3^+$ 29%), 122 ($C_3H_7PO_3^+$ 44%), 97 ($C_6H_9O^+$ 18%), 79 (PO_3^+ 13%), 29 ($C_2H_5^+$ 20%), 15 (CH_3^+ 1%); IR ν/cm^{-1} 1708 (s; C=O), 1251 (s; P=O).

Diethyl 3-(2-Methyl-3-oxocyclohexyl)prop-1-enylphosphonate **5c**. Colorless oil purified by bulb-to-bulb distillation (oven temp. 175°C/0.04 mmHg) yielding (1.14 g, 70.3%) of two isomers (approximately 1:1). Isomer A ^{1}H NMR δ 1.04 (3H; d; J_{HH} 6.6

Hz; CH_3 on C(2)); 1.28 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^a); 1.29 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^b); 1.45–1.84 (3H; m; CH on C(5), CH on C(6), CH on C(1)); 1.85–2.17 (3H; m; CH on C(5), CH on C(6), CH on C(2)); 2.19–2.60 (4H; m; CH_2 on C(4), γ-CH_2); 4.02 (2H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH_2 of POEt^a); 4.03 (2H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH_2 of POEt^b); 5.69 (1H; d of d; J_{HP} 21.3 Hz; J_{HH} 16.3 Hz; α-CH); 6.70 (1H; m; β-CH); ^{31}P NMR δ 18.28; ^{13}C NMR δ 11.28 (q; J_{CH} 125.2 Hz; CH_3 on C(2)); 15.69 (q; J_{CH} 126.6 Hz; 2 × CH_3 of POEt); 24.87 (t; J_{CH} 129.6 Hz; CH_2 on C(5)); 29.88 (t; J_{CH} 129.1 Hz; CH_2 on C(6)); 38.09 (d of t; J_{CP} 22.3 Hz; J_{CH} 138.7 Hz; γ-CH_2); 40.61 (t; J_{CH} 127.8 Hz; CH_2 on C(4)); 44.00 (d; J_{CH} 129.6 Hz; CH on C(1)); 48.73 (d; J_{CH} 119.8 Hz; CH on C(2)); 60.93 (t; J_{CH} 147.5 Hz; 2 × CH_2 of POEt); 119.14 (d of d; J_{CP} 184.7 Hz; J_{CH} 157.0 Hz; α-CH); 149.72 (d; J_{CH} 152.1 Hz; β-CH); 211.19 (s; C of C(3)); isomer B ^{1}H NMR δ 1.00 (3H; d; J_{HH} 7.0 Hz; CH_3 on C(2)); 1.28 (3H; t; J_{HH} 7.0 Hz CH_3 of POEt^a); 1.29 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^b); 1.45–1.84 (3H; m; CH on C(5), CH on C(6), CH on C(1)); 1.85–2.17 (3H; m; CH on C(5), CH on C(6), CH on C(2)); 2.19–2.60 (4H; m; CH_2 on C(4), γ-CH_2); 4.02 (2H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH_2 of POEt^a); 4.03 (2H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; CH_2 of POEt^b); 5.69 (1H; d of d; J_{HP} 21.3 Hz; J_{HH} 16.3 Hz;α-CH); 6.70 (1H; m; β-CH); ^{31}P NMR δ 18.33; ^{13}C NMR δ 10.91 (q; J_{CH} 125.2 Hz; CH_3 on C(2)); 15.69 (q; J_{CH} 126.6 Hz; 2 × CH_3 of POEt); 22.79 (t; J_{CH} 129.6 Hz; CH_2 on C(5)); 25.60 (t; J_{CH} 129.1 Hz; CH_2 on C(6)); 33.30 (d of t; J_{CP} 22.0 Hz; J_{CH} 138.7 Hz; γ-CH_2); 40.84 (t; J_{CH} 127.8 Hz; CH_2 on C(4)); 44.00 (d; J_{CH} 129.6 Hz; CH on C(1)); 47.88 (d; J_{CH} 119.8 Hz; CH on C(2)); 60.93 (t; J_{CH} 147.5 Hz; 2 × CH_2 of POEt); 118.47 (d of d; J_{CP} 185.5 Hz; J_{CH} 157.0 Hz; α-CH); 150.47 (d; J_{CH} 152.1 Hz; β-CH); 211.19 (s; C of C(3)); MS *m/z* 289 ((M + 1)$^+$ 2%), 288$^+$ 1%), 178 ($C_7H_{15}PO_3^+$ 100%), 110 ($C_7H_{10}O^+$3%), 79 (PO_3^+ 8%), 29 ($C_2H_5^+$ 19%), 15 (CH$^+$3 1%); IR ν/cm^{-1} 1706 (s; C=O), 1236 (s; P=O); anal. calcd for $C_{14}H_{25}PO_4$ (288.32): C, 58.32; H, 8.74. Found: C, 57.75; H, 8.10.

Diethyl 1-(1-Hydroxy-3-methylcyclohex-2-enyl) prop-2-enylphosphonate **3g**. Colorless oil purified by column chromatography (EtOAc) (1.88 g, 77.5%) ^{1}H NMR δ 1.28 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^a); 1.30 (3H; t; J_{HH} 7.0 Hz; CH_3 of POEt^b); 1.57–1.64 (2H; m; CH_2 on C(5)); 1.61 (3H; s; CH_3 on C(3)); 1.76–1.82 (4H; m; CH_2 on C(4), CH_2 on C(6)); 2.73 (1H; d of d of t; J_{HP} 19.6 Hz; $J_{H\alpha H\beta}$ 9.6 Hz; $J_{H\alpha H\gamma}$ 1.5 Hz; α-CH); 4.08 (2H; quint; J_{HP} 7.7 Hz; J_{HH} 7.3 Hz; CH_2 of POEt^a); 4.11 (2H; quint; J_{HP} 7.7 Hz; J_{HH} 7.3 Hz; CH_2 of POEt^b); 4.25 (1H; s; OH); 5.13 (2H; m; γ-CH_2); 5.26 (1H; s; CH on C(2)); 5.59 (1H; m; β-CH); ^{31}P NMR δ 28.83; ^{13}C NMR δ 16.01 (q; J_{CH} 125.3 Hz; CH_3 of POEt^a); 16.09 (q; J_{CH} 125.3 Hz; CH_3 of POEt^b); 18.30 (t; J_{CH} 129.6 Hz; CH_2 on C(5)); 23.37 (q; J_{CH} 125.7 Hz; CH_3 on C(3)); 29.46 (t; J_{CH} 123.4 Hz; CH_2 on C(4)); 32.69 (d of t; J_{CP} 6.0 Hz; J_{CH} 124.6 Hz; CH_2 on C(6)); 53.90 (d of d; J_{CP} 131.4 Hz; J_{CH} 128.7 Hz; α-CH); 61.79 (t; J_{CH} 151.5 Hz; CH_2 of POEt^a); 61.95 (t; J_{CH} 151.5 Hz; CH_2 of POEt^b); 70.32 (d; J_{CP} 3.0 Hz; C of C(1)); 119.80 (d of t; J_{CP} 12.8 Hz; J_{CH} 156.8 Hz; γ-CH_2); 126.00 (d of d; J_{CP} 14.4 Hz; J_{CH} 156.9 Hz; CH on C(2)); 130.49 (d of d; J_{CP} 9.5 Hz; J_{CH} 158.2 Hz; β-CH); 137.86 (s; C of C(3)); MS *m/z* 290 ((M + 1)$^+$ <1%), 270 ($C_{14}H_{23}PO_3^+$ 100%), 269 ($C_{14}H_{22}PO_3^+$ 23%), 213 ($C_{10}H_{14}PO_3^+$ 14%), 178 ($C_7H_{15}PO_3^+$ 36%), 150 ($C_5H_{11}PO_3^+$ 15%), 132 ($C_{10}H_{12}^+$ 93%), 131 ($C_{10}H_{11}^+$ 100%), 122 ($C_3H_7PO_3^+$ 42%), 111 ($C_7H_{11}O^+$ 23%), 79 (PO_3^+ 10%), 29 ($C_2H_5^+$ 21%), 15 (CH_3^+ 2%); IR ν/cm^{-1} 1225 (s; P=O), 3413 (s; OH); anal. calcd for $C_{14}H_{25}PO_4$ (288.32): C, 58.32; H, 8.74. Found: C, 57.54; H, 9.14.

Wadsworth–Emmons Reaction of 3g

The alcohol (1 mol equiv.) reacted with NaH (2 mol equiv.) in DMF (11 mL/mmol of alcohol) according to a standard procedure to give the expected triene. This product proved to be very volatile, and no yield could be accurately determined. No attempts were made to determine the configuration of the product.

3-Allylidene-1-methyl-cyclohexene. ^{1}H NMR δ 1.70 (2H; t; J_{HH} 6.3 Hz; CH_2 on C(6)); 1.75 (3H; s; CH_3 on C(1)); 2.03 (2H; t; J_{HH} 6.2 Hz; CH_2 on C(4)); 2.37 (2H; m; CH_2 on C(5)); 4.97 (1H; d of d; $J_{H\gamma H\beta}$ 10.1 Hz; $J_{H\gamma H\alpha}$ 1.6 Hz; γ-CH); 5.09 (1H; d of d; $J_{H\gamma H\beta}$ 16.6 Hz; $J_{H\gamma H\alpha}$ 1.6 Hz; γ-CH); 5.76 (1H; d; J_{HH} 11.3 Hz; α-CH); 5.84 (1H; s; CH on C(2)); 6.61 (1H; d of d of d; $J_{H\beta H\gamma}$ 16.9 Hz; $J_{H\beta H\gamma}$ 10.7 Hz; $J_{H\beta H\alpha}$ 10.6 Hz; β-CH); ^{13}C NMR δ 22.53; (t; J_{CH} 127.7 Hz; CH_2 on C(4)); 23.96 (q; J_{CH} 126.0 Hz; CH_3 on C(1)); 24.32 (q; J_{CH} 126.0 Hz; CH_3 on C(1)); 24.83 (t; J_{CH} 127.5 Hz; CH_2 on C(5)); 29.63 (t; J_{CH} 124.7 Hz; CH_2 on C(6)); 30.64 (t; J_{CH} 124.2 Hz; CH_2 on C(5)); 30.75 (t; J_{CH} 124.2 Hz; CH_2 on C(6)); 36.92 (t; J_{CH} 126.1 Hz; CH_2 on C(4)); 114.87 (t; J_{CH} 159.5 Hz; γ-CH_2); 124.35 (d; J_{CH} 150.3 Hz; α-CH); 126.53 (d; J_{CH} 160.3 Hz; CH on C(2)); 126.65 (d; J_{CH} 160.3 Hz; CH on C(2)); 128.06 (s; C of C(1)); 132.97 (d; J_{CH} 150.8 Hz; β-CH); 149.68 (s; C of C(3)); MS *m/z* 135 ((M + 1)$^+$ 10%), 134 (M$^+$ 75%), 119 ($C_9H_{11}^+$ 61%), 105 ($C_8H_9^+$) 38%), 91 ($C_7H_7^+$ 100%), 29 ($C_2H_5^+$ 4%);

Dehydration of Tertiary Alcohols 3 *under Kinetic Conditions. General Procedure*

The alcohol (1 mol equiv.) was dissolved in benzene (ca. 4 mL/mmol of alcohol) containing TsOH (0.08

mol equiv.). This mixture was stirred at room temperature for 24 hours. The mixture was washed with an aqueous solution of $NaHCO_3$ and then with water. The organic layer was dried over $MgSO_4/Na_2SO_4$, filtered, and the solvent was removed under reduced pressure. The crude products were purified as shown for each individual compound.

Dehydration of 3g gave diethyl 1-(3-methylenecyclohex-2-enyl)prop-2-enylphosphonate 7 (0.89 g, 72.1%); ^{1}H NMR δ 1.18 (6H; m; 2 × CH_3 of POEt); 1.61 (2H; m; CH_2 on C(5)); 1.98–2.21 (4H; m; CH_2 on C(4), CH_2 on C(6)); 3.18 (1H; d of d; J_{HP} 25.1 Hz; $J_{H\alpha H\beta}$ 8.2 Hz; α-CH); 3.99 (4H; m; 2 × CH_2 of POEt); 4.64 (1H; s; CH of CH_2 on C(3)); 4.66 (1H; s; CH′ of CH_2 on C(3)); 5.18 (2H; m; γ-CH_2); 5.88 (1H; m; β-CH); 6.06 (1H; s; CH on C(2)); ^{31}P NMR δ 25.58; 25.54; ^{13}C NMR δ 16.29 (q; J_{CH} 127.8 Hz; CH_3 of POEt^a); 16.37 (q; J_{CH} 127.8 Hz; CH_3 of POEt^b); 23.05 (t; J_{CH} 128.4 Hz; CH_2 on C(5)); 28.28 (t; J_{CH} 132.4 Hz; CH_2 on C(6)); 30.02 (t; J_{CH} 132.5 Hz; CH_2 on C(4)); 51.39 (d of d; J_{CP} 135.8 Hz; J_{CH} 131.3 Hz; α-CH); 62.21 (t; J_{CH} 145.9 Hz; CH_2 of POEt^a); 62.30 (t; J_{CH} 145.9 Hz; CH_2 of POEt^b); 110.58 (t; J_{CH} 156.1 Hz; CH_2 on C(3)); 118.53 (t; J_{CH} 157.5 Hz; γ-CH_2); 126.84 (d of d; J_{CP} 12.9 Hz; J_{CH} 148.5 Hz; CH on C(2)); 128.76 (d of d; J_{CP} 12.1 Hz; J_{CH} 148.5 Hz; β-CH); 136.08 (s; C of C(3)); 142.93 (s; C of C(1)); MS *m/z* 270 (M^+ 13%), 133 ($C_{10}H_{13}^+$ 13%), 131 ($C_{10}H_{11}^+$ 100%), 91 ($C_7H_7^+$ 37%), 79 (PO_3^+ 9%), 29 ($C_2H_5^+$ 21%), 15 (CH_3^+ 3%).

Dehydration of 3b. Colorless oil purified by column chromatography (EtOAc) yielding two products. Diethyl(cyclohex-2-enylidene)methylphosphonate **8d** (0.074 g, 7.4%),; ^{1}H NMR δ 1.28 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.73 (2H; d of d of d of d; J_{HH} 5.1 Hz; CH_2 on C(5)); 2.15 (2H; m; CH_2 on C(6)); 2.39 (2H; m; CH_2 on C(4)); 4.05 (4H; quint; J_{HP} 7.3 Hz; J_{HH} 7.3 Hz; 2 × CH_3 of POEt); 5.18 (1H; d; J_{HP} 17.5 Hz; α-CH); 6.16 (1H; mħ on C(3)); 7.02 (1H; d; J_{HH} 10.2 Hz; CH on C(2)); ^{31}P NMR δ 18.49; ^{13}C NMR δ 16.27 (q; J_{CH} 126.5 Hz; CH_3 of POEt^a); 16.36 (q; J_{CH} 126.5 Hz; CH_3 of POEt^b); 22.48 (t; J_{CH} 124.4 Hz; CH_2 on C(5)); 25.64 (t; J_{CH} 126.9 Hz; CH_2 on C(4)); 33.73 (d of t; J_{CP} 22.3 Hz; J_{CH} 128.2 Hz; CH_2 on C(6)); 61.22 (t; J_{CH} 144.5 Hz; CH_2 of POEt^a); 61.28 (t; J_{CH} 144.5 Hz; CH_2 of POEt^b); 109.22 (d of d; J_{CP} 186.8 Hz; J_{CH} 154.9 Hz; α-CH); 125.65 (d of d; J_{CP} 8.8 Hz; J_{CH} 157.6 Hz; CH on C(2)); 137.48 (d; J_{CH} 157.5 Hz; CH on C(3)); 155.89 (s; C of C(1)); MS *m/z* 231 ($(M + 1)^+$ 11%), 230 (M^+ 43%), 201 ($C_9H_{14}PO_3^+$ 22%), 173 ($C_7H_{10}PO_3^+$ 49%), 93 ($C_7H_9^+$ 38%), 92 ($C_7H_8^+$ 92%), 91 ($C_7H_7^+$ 100%), 79 (PO_3^+ 28%), 29 ($C_2H_5^+$ 42%), 15 (CH_3^+ 6%); anal. calcd for $C_{11}H_{19}PO_3$ (230.24): C, 57.38; H, 8.32. Found: C, 58.01; H, 8.96.

Diethyl(3-hydroxycyclohex-1-enyl)methylphosphonate 10. (0.48 g, 45.0%). ^{1}H NMR δ 1.24 (6H; t; J_{HH} 7.0 Hz; 2 × CH_3 of POEt); 1.52 (2H; m; CH_2 on C(6)); 1.70 (2H; m; CH_2 on C(5)); 2.05 (2H; m; CH_2 on C(4)); 2.46 (2H; m; α-CH_2); 3.93 (1H; m; CH on C(3)); 4.01 (4H; m; 2 × CH_2 of POEt); 5.59 (1H; s; CH on C(2)); ^{31}P NMR δ 27.89; ^{13}C NMR δ 16.31 (q; J_{CH} 125.6 Hz; CH_3 of POEt^a); 16.39 (q; J_{CH} 125.6 Hz; CH_3 of POEt^b); 19.30 (d of t; J_{CP} 19.4 Hz; J_{CH} 128.6 Hz; CH_2 on C(5)); 28.65 (d of t; J_{CP} 31.3 Hz; J_{CH} 128.3 Hz; CH_2 on C(6)); 29.52 (t; J_{CH} 127.1 Hz; CH_2 on C(4)); 35.17 (d of t; J_{CP} 137.2 Hz; J_{CH} 130.3 Hz; α-CH_2); 61.75 (t; J_{CH} 147.2 Hz; CH_2 of POEt^a); 61.84 (t; J_{CH} 147.2 Hz; CH_2 of POEt^b); 70.73 (d; J_{CH} 140.7 Hz; CH on C(3)); 127.85 (d of d; J_{CP} 11.4 Hz; J_{CH} 158.0 Hz; CH on C(2)); 132.45 (d; J_{CP} 10.5 Hz; C of C(1)); MS *m/z* 248 (M^+ <1%), 230 ($C_{11}H_{19}PO_3^+$ 40%), 229 ($C_{11}H_{18}PO_3^+$ 76%), 201 ($C_9H_{14}PO_3^+$ 33%), 173 ($C_7H_{10}PO_3^+$ 92%), 91 ($C_7H_7^+$ 100%), 29 ($C_2H_5^+$ 26%), 15 (CH_3^+ 3%); anal. calcd for $C_{11}H_{20}PO_4$ (247.25): C, 53.22; H, 8.53. Found: C, 52.68; H, 8.01.

Dehydration of Tertiary Alcohols 3 *under Thermodynamic Conditions*

The alcohol (1 mol equiv.) was dissolved in benzene (ca. 4 mL/mmol of alcohol) containing TsOH (0.08 mol equiv.). This mixture was refluxed for 7 hours. The mixture was washed with an aqueous solution of $NaHCO_3$ and then with water. The organic layer was dried over $MgSO_4/Na_2SO_4$, filtered, and the solvent was removed under reduced pressure. The crude products were purified as shown for each individual compound.

Dehydration of 3g. Colorless oil purified by column chromatography (EtOAc) giving two isomers of **8a**. (*Z*) Diethyl 1-(3-methylcyclohexen-2-enylidene)prop-2-enylphosphonate (0.16 g, 28.6%) ^{1}H NMR δ 1.28 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.69 (2H; d of d of d of d; J_{H5H4} 6.0 Hz; J_{H5H6} 5.4 Hz; CH_2 on C(5)); 1.84 (3H; s; CH_3 on C(3)); 2.07 (2H; d of d; J_{HH} 6.0 Hz; CH_2 on C(4)); 2.45 (2H; m; CH_2 on C(6)); 4.02 (4H; m; 2 × CH_2 of POEt); 5.26 (1H; d of d of d; J_{HH} 15.1 Hz; $J_{H\gamma H\beta}$ 14.6 Hz; J_{HP} 2.2 Hz; γ-CH_a); 5.27 (1H; d of d of d; J_{HH} 15.1 Hz; $J_{H\gamma H\beta}$ 9.4 Hz; J_{HP} 2.2 Hz; γ-CH_b); 6.39 (1H; m; β-CH); 7.14 (1H; m; CH on C(2)); ^{31}P NMR δ 19.35; ^{13}C NMR δ 16.19 (q; J_{CH} 127.1 Hz; CH_3 of POEt^a); 16.27 (q; J_{CH} 127.1 Hz; CH_3 of POEt^b); 22.54 (t; J_{CH} 128.0 Hz; CH_2 on C(5)); 24.88 (q; J_{CH} 122.4 Hz; CH_3 on C(3)); 28.38 (d of t; J_{CP} 16.5 Hz; J_{CH} 126.5 Hz; CH_2 on C(6)); 30.69 (t; J_{CH} 124.5 Hz; CH_2 on C(4)); 61.21 (t; J_{CH} 144.7 Hz; CH_2 of POEt^a); 61.27 (t; J_{CH} 144.7 Hz; CH_2 of POEt^b); 118.96 (d of t; J_{CP} 8.2 Hz; J_{CH} 158.0 Hz; γ-CH_2); 123.24 (d of d; J_{CP} 8.3 Hz; J_{CH} 156.4 Hz; CH on C(2)); 132.95 (d of d; J_{CP} 9.7 Hz; J_{CH} 156.9 Hz; β-CH); 146.46 (s; C of C(3)); 152.04 (d; J_{CP} 9.6 Hz; α-C); 152.05 (d; J_{CP} 9.6 Hz; C of C(1)); MS *m/z* 271 ((M + 1)$^+$ 4%), 270 (M$^+$ 17%), 213 ($C_{10}H_{14}PO_3^+$ 6%), 132 ($C_{10}H_{12}^+$ 100%), 105 ($C_8H_9^+$ 25%), 91 ($C_7H_7^+$ 93%), 79 (PO_3^+ 13%), 29 ($C_2H_5^+$ 15%), 15 (CH_3^+ 1%); Anal. calcd for $C_{14}H_{23}PO_3$ (270,31): C, 62.21; H, 8.58. Found: C, 61.99; H, 8.35.

(E) Diethyl 1-(3-Methylcyclohex-2-enylidene) prop-2-enylphosphonate (0.15 g, 28.1%). ^{1}H NMR δ 1.26 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.71 (2H; d of d of d of d; J_{H5H4} 6.2 Hz; J_{H5H6} 5.7 Hz; CH_2 on C(5)); 1.79 (3H; s; CH_3 on C(3)); 2.05 (2H; d of d; J_{HH} 6.1 Hz; CH_2 on C(4)); 2.74 (2H; m; CH_2 on C(6)); 4.02 (4H; m; 2 × CH_2 of POEt); 5.26 (1H; d of d of d; J_{HH} 16.4 Hz; $J_{H\gamma H\beta}$ 16.7 Hz; J_{HP} 2.2 Hz; γ-CH_a); 5.27 (1H; d of d of d; J_{HH} 16.7 Hz; $J_{H\gamma H\beta}$ 9.4 Hz; J_{HP} 2.2 Hz; γ-CH_b); 6.39 (1H; m; β-CH); 7.14 (1H; m; CH on C(2)); ^{31}P NMR δ 20.08; ^{13}C NMR δ 16.21 (q; J_{CH} 127.0 Hz; CH_3 of POEt^a); 16.30 (q; J_{CH} 127.0 Hz; CH_3 of POEt^b); 22.66 (t; J_{CH} 128.3 Hz; CH_2 on C(5)); 24.63 (q; J_{CH} 125.5 Hz; CH_3 on C(3)); 28.41 (d of t; J_{CP} 6.6 Hz; J_{CH} 128.8 Hz; CH_2 on C(6)); 30.83 (t; J_{CH} 124.9 Hz; CH_2 on C(4)); 61.21 (t; J_{CH} 144.6 Hz; CH_2 of POEt^a); 61.28 (t; J_{CH} 144.6 Hz; CH_2 of POEt^b); 120.05 (d of t; J_{CP} 9.4 Hz; J_{CH} 158.0 Hz; γ-CH_2); 122.70 (d of d; J_{CP} 20.7 Hz; J_{CH} 133.1 Hz; CH on C(2)); 132.68 (d of d; J_{CP} 9.6 Hz; J_{CH} 156.1 Hz; β-CH); 143.58 (d; J_{CP} 10.3 Hz; C of C(1)); 146.55 (s; C of C(3)); 151.48 (d; J_{CP} 11.8 Hz; α-C); MS *m/z* 271 ((M + 1)$^+$ 7%), 270 (M$^+$ 34%), 213 ($C_{10}H_{14}PO_3^+$ 43%), 131 ($C_{10}H_{11}^+$ 100%), 105 ($C_8H_9^+$ 12%), 79 (PO_3^+ 7%), 29 ($C_2H_5^+$ 13%), 15 (CH_3^+ 1%); anal. calcd for $C_{14}H_{23}PO_3$ (270.31): C, 62.21; H, 8.58. Found: C, 63.14; H, 8.58.

Dehydration of **3e**. Colorless oil purified by column chromatography (EtOAc) giving two isomers of diethyl (3-methylcyclohex-2-enylidene)methylphosphonate **8b**; *Z*-isomer (0.30 g, 18.5%), ^{1}H NMR δ 1.25 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.69 (2H; d of d of d of d; J_{HH} 6.1 Hz; CH_2 on C(5)); 1.79 (3H; s; CH_3 on C(3)); 2.05 (2H; d of d; J_{HH} 6.0 Hz; CH_2 on C(4)); 2.29 (2H; m; CH_2 on C(6)); 3.99 (4H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; 2 × CH_2 of POEt); 5.03 (1H; d; J_{HP} 17.6 Hz; α-CH); 6.80 (1H; s; CH on C(2)); ^{31}P NMR δ 19.29; ^{13}C NMR δ 15.84 (q; J_{CH} 126.9 Hz; CH_3 of POEt^a); 15.92 (q; J_{CH} 126.9 Hz; CH_3 of POEt^b); 22.17 (t; J_{CH} 128.5 Hz; CH_2 on C(5)); 24.07 (q; J_{CH} 126.3 Hz; CH_3 on C(3)); 30.33 (t; J_{CH} 126.3 Hz; CH_2 on C(4)); 32.90 (d of t; J_{CP} 22.5 Hz; J_{CH} 128.4 Hz; CH_2 on C(6)); 60.64 (t; J_{CH} 146.6 Hz; CH_2 of POEt^a); 60.71 (t; J_{CH} 146.6 Hz; CH_2 of POEt^b); 105.83 (d of d; J_{CP} 187.8 Hz; J_{CH} 154.2 Hz; α-CH); 121.29 (d of d; J_{CP} 9.1 Hz; J_{CH} 158.0 Hz; CH on C(2)); 147.08 (s; C of C(3)); 156.33 (d; J_{CP} 5.1 Hz; C of C(1)); MS *m/z* 245 ((M + 1)$^+$ 10%), 244 (M$^+$ 30%), 187 ($C_8H_{12}PO_3^+$ 30%), 106 ($C_8H_{10}^+$ 58%), 105 ($C_8H_9^+$ 100%), 91 ($C_7H_7^+$ 58%), 79 (PO_3^+ 39%), 29 ($C_2H_5^+$ 33%), 15 (CH_3^+ 4%); anal. calcd for $C_{12}H_{21}PO_3$ (244.27): C, 56.93; H, 8.45. Found: C, 56.64; H, 8.66.

E-Isomer of **8b** *(0.39 g, 24.4%).* ^{1}H NMR δ 1.25 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.68 (2H; m; CH_2 on C(5)); 1.76 (3H; s; CH_3 on C(3)); 2.03 (2H; d of d; J_{HH} 6.0 Hz; CH_2 on C(4)); 2.64 (2H; m; CH_2 on C(6)); 3.97 (4H; quint; J_{HP} 7.1 Hz; J_{HH} 7.1 Hz; 2 × CH_2 of POEt); 5.11 (1H; d; J_{HP} 18.2 Hz; α-CH); 5.86 (1H; s; CH on C(2)); ^{31}P NMR δ 20.49; ^{13}C NMR δ 15.81 (q; J_{CH} 126.9 Hz; CH_3 of POEt^a); 15.89 (q; J_{CH} 126.9 Hz; CH_3 of POEt^b); 21.79 (t; J_{CH} 128.6 Hz; CH_2 on C(5)); 23.66 (q; J_{CH} 126.3 Hz; CH_3 on C(3)); 26.69 (d of t; J_{CP} 6.3 Hz; J_{CH} 126.6 Hz; CH_2 on C(6)); 29.94 (t; J_{CH} 123.7 Hz; CH_2 on C(4)); 60.57 (t; J_{CH} 146.8 Hz; CH_2 of POEt^a); 60.63 (t; J_{CH} 146.8 Hz; CH_2 of POEt^b); 107.29 (d of d; J_{CP} 193.0 Hz; J_{CH} 151.6 Hz; α-CH); 125.82 (d of d; J_{CP} 27.7 Hz; J_{CH} 155.8 Hz; CH on C(2)); 146.33 (s; C of C(3)); 156.93 (d; J_{CP} 8.2 Hz; C of C(1)); MS *m/z* 245 ((M + 1)$^+$ 16%), 244 (M$^+$ 61%), 187 ($C_8H_{12}PO_3^+$ 37%), 106 ($C_8H_{10}^+$ 87%), 105 ($C_8H_9^+$ 100%), 91 ($C_7H_7^+$ 71%), 79 (PO_3^+ 33%), 29 ($C_2H_5^+$ 43%), 15 (CH_3^+ 6%); anal. calcd for $C_{12}H_{21}PO_3$ (244.27): C, 56.93; H, 8.45. Found: C, 56.64; H, 8.66.

Dehydration of **3d** *gave (E) diethyl (2-methylcyclohex-2-enylidene)methylphosphonate* **8c**. *Colorless oil purified by column chromatography (EtOAc) (0.074 g, 79.5%).* ^{1}H NMR δ 1.27 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.68 (2H; d of d of d of d; J_{HH} 6.3 Hz; CH_2 on C(5)); 1.78 (3H; s; CH_3 on C(2)); 2.14 (2H; m; CH_2 on C(4)); 2.74 (2H; m; CH_2 on C(6)); 4.04 (4H; quint; J_{HP} 7.3 Hz; J_{HH} 7.1 Hz; 2 × CH_2 of POEt); 5.38 (1H; d; J_{HP} 17.0 Hz; α-CH); 5.98 (1H; m; CH on C(3)); ^{31}P NMR δ 20.88; ^{13}C NMR δ 16.16 (q; J_{CH} 126.1 Hz; CH_3 of POEt^a); 16.24 (q; J_{CH} 126.1 Hz; CH_3 of POEt^b); 19.60 (q; J_{CH} 126.6 Hz; CH_3 on C(2)); 22.39 (t; J_{CH} 147.1 Hz; CH_2 on C(5)); 26.01 (t; J_{CH} 128.4 Hz; CH_2 on C(4)); 28.63 (d of t; J_{CP} 6.9 Hz; J_{CH} 135.3 Hz; CH_2 on C(6)); 61.14 (t; J_{CH} 146.9 Hz; CH_2 of POEt^a); 61.21 (t; J_{CH} 146.9 Hz; CH_2 of POEt^b); 107.41 (d of d; J_{CP} 192.7 Hz; J_{CH} 153.7 Hz; α-CH); 132.56 (d; J_{CP} 23.9 Hz; C of C(2)); 134.99 (d; J_{CH} 159.2 Hz; CH on C(3)); 157.86 (d; J_{CP} 8.8 Hz; C of C(1)); MS *m/z* 244 (M$^+$ 4%), 91 ($C_7H_7^+$ 31%), 79 (PO_3^+ 19%), 29 ($C_2H_5^+$ 17%), 15 (CH_3^+ 4%).

Dehydration of **3b**. Colorless oil purified by column chromatography (EtOAc) yielding (*E*/*Z*) diethyl (cyclohex-2-enylidene)methylphosphonate **8d** (0.48 g, 36.8%). ^{1}H NMR δ 1.28 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3

of POEt); 1.73 (2H; d of d of d of d; J_{HH} 5.1 Hz; CH_2 on C(5)); 2.15 (2H; m; CH_2 on C(6)); 2.39 (2H; m; CH_2 on C(4)); 4.05 (4H; quint; J_{HP} 7.3 Hz; J_{HH} 7.3 Hz; 2 × CH_3 of POEt); 5.18 (1H; d; J_{HP} 17.5 Hz; α-CH); 6.16 (1H; m; CH on C(3)); 7.02 (1H; d; J_{HH} 10.2 Hz; CH on C(2)); ^{31}P NMR δ 18.49; ^{13}C NMR δ 16.27 (q; J_{CH} 126.5 Hz; CH_3 of POEt^a); 16.36 (q; J_{CH} 126.5 Hz; CH_3 of POEt^b); 22.48 (t; J_{CH} 124.4 Hz; CH_2 on C(5)); 25.64 (t; J_{CH} 126.9 Hz; CH_2 on C(4)); 33.73 (d of t; J_{CP} 22.3 Hz; J_{CH} 128.2 Hz; CH_2 on C(6)); 61.22 (t; J_{CH} 144.5 Hz; CH_2 of POEt^c); 61.28 (t; J_{CH} 144.5 Hz; CH_2 of POEt^b); 109.22 (d of d; J_{CP} 186.8 Hz; J_{CH} 154.9 Hz; α-CH); 125.65 (d of d; J_{CP} 8.8 Hz; J_{CH} 157.6 Hz; CH on C(2)); 137.48 (d; J_{CH} 157.5 Hz; CH on C(3)); 155.89 (s; C of C(1)); MS *m/z* 231 ((M + 1)$^+$ 11%), 230 (M$^+$ 43%), 201 ($C_9H_{14}PO_3^+$ 22%), 173 ($C_7H_{10}PO_3^+$ 49%), 93 ($C_7H_9^+$ 38%), 92 ($C_7H_8^+$ 92%), 91 ($C_7H_7^+$ 100%), 79 (PO_3^+ 28%), 29 ($C_2H_5^+$ 42%), 15 (CH_3^+ 6%); anal. calcd for $C_{11}H_{19}PO_3$ (230,24): C, 57.38; H, 8.32. Found: C, 58.01; H, 7.96.

Oxidation of 10

10 (0.208g, 0.839 mmol) was dissolved in 30 mL of chloroform. Neutral activated manganese dioxide was prepared just prior to the reaction, according to the literature method [21]; 2.949 g (33.9 mmol) of the oxide was added and the mixture stirred for 4 hours at room temperature. The mixture was filtered through celite and the solvent removed under reduced pressure to yield a crude, yellow oil. This oil was purified by column chromatography (EtOAc) yielding diethyl (3-oxocyclohex-1-enyl)methylphosphonate 11 (0.087 g, 42.2%). The silica gel used for the separation was deactivated first by pouring wet ether containing 1% acetic acid through it and then allowing the ether to evaporate. ^{1}H NMR δ 1.22 (6H; t; J_{HH} 7.1 Hz; 2 × CH_3 of POEt); 1.91 (2H; t of t; J_{HH} 6.0 Hz; CH_2 on C(5)); 2.26 (2H; t; J_{HH} 6.0 Hz; CH_2 on C(4)); 2.38 (2H; d of t; J_{HP} 3.8 Hz; J_{HH} 5.7 Hz; CH_2 on C(6)); 2.66 (2H; d; J_{HP} 23.6 Hz; α-CH_2); 4.01 (4H; quint; J_{HP} 7.4 Hz; J_{HH} 7.4 Hz; 2 × CH_2 of POEt); 5.85 (1H; d; J_{HP} 4.9 Hz; CH on C(2)); ^{31}P NMR δ 24.22; ^{13}C NMR δ 16.18 (q; J_{CH} 126.5 Hz; CH_3 of POEt^a); 16.26 (q; J_{CH} 126.5 Hz; CH_3 of POEt^b); 22.39 (t; J_{CH} 129.4 Hz; CH_2 on C(5)); 30.31 (t; J_{CH} 128.1 Hz; CH_2 on C(6)); 36.05 (d of t; J_{CP} 134.9 Hz; J_{CH} 127.5 Hz; α-CH_2); 36.80 (t; J_{CH} 127.8 Hz; CH_2 on C(4)); 62.14 (t; J_{CH} 150.6 Hz; CH_2 of POEt^a); 62.23 (t; J_{CH} 150.6 Hz; CH_2 of POEt^b); 129.19 (d of d; J_{CP} 11.1 Hz; J_{CH} 161.7 Hz; CH on C(2)); 155.95 (d; J_{CP} 11.0 Hz; C of C(1)); 198.80 (s; C of C(3)); MS *m/z* 246 (M$^+$ 19%), 189 ($C_7H_{10}PO_4^+$ 26%), 108 ($C_7H_8O^+$ 100%), 79(PO_3^+ 22%), 29 ($C_2H_5^+$ 11%), 15 (CH_3^+ 1%); IR $h\upsilon$/cm^{-1} 1667 (s; C=0), 1257 (s; P=0); anal. calcd for $C_{11}H_{19}PO_4$ (246,24):C, 53.65; H, 7.78. Found: C, 53.79; H, 8.54.

Reaction of 3b *with Methanol*

3b was dissolved in 30 mL of methanol. This mixture was kept at reflux temperature for 3 hours, cooled, and the solvent removed under reduced pressure. The residue was dissolved in chloroform, dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure to yield diethyl (3-methoxycyclohex-1-enyl)methylphosphonate 12, 0.479 g (100%) as a yellow oil. ^{1}H NMR δ 1.27 (6H; t; J_{HH} 7.2 Hz; 2 × CH_3 of POEt); 1.55 (2H; m; CH_2 on C(5)); 1.72 (2H; m; CH_2 on C(6)); 2.08 (2H; m; CH_2 on C(4)); 2.45 (1H; d of d; J_{HP} 22.0 Hz; J_{HH} 14.9 Hz; CH^a of α-CH_2); 2.51 (1H; d of d; J_{HP} 22.0 Hz; J_{HH} 14.9 Hz; CH^b of α-CH_2); 3.31 (3H; s; CH_3 of OMe); 3.72 (1H; m; CH on C(3)); 4.05 (4H; quint; J_{HP} 7.2 Hz; J_{HH} 7.2 Hz; 2 × CH_2 of POEt); 5.68 (1H; m; CH on C(2)); ^{31}P NMR δ 27.69; ^{13}C NMR δ 15.81 (q; J_{CH} 127.7 Hz; CH_3 of POEt^a); 15.89 (q; J_{CH} 127.7 Hz; CH_3 of POEt^a); 18.74 (t; J_{CH} 128.3 Hz; CH_2 on C(5)); 26.76 (t; J_{CH} 127.3 Hz; CH_2 on C(6)); 29.10 (t; J_{CH} 125.9 Hz; CH_2 on C(4)); 34.64 (d of t; J_{CP} 137.2 Hz; J_{CH} 131.2 Hz; α-CH_2); 55.07 (q; J_{CH} 140.4 Hz; CH_3 of OMe); 61.01 (t; J_{CH} 147.3 Hz; CH_2 of POEt^a); 61.25 (t; J_{CH} 147.3 Hz; CH_2 of POEt^b); 73.83 (d; J_{CH} 141.4 Hz; CH on C(3)); 126.27 (d of d; J_{CP} 12.5 Hz; J_{CH} 153.4 Hz; CH on C(2)); 132.40 (d; J_{CP} 10.3 Hz; C of C(1)); MS *m/z* 246 ((M − 15)$^+$ <1%), 229 ($C_{11}H_{18}PO_3^+$ 70%), 173 ($C_7H_{10}PO_3^+$ 61%), 124 ($C_8H_{12}O^+$ 100%), 91 ($C_7H_7^+$ 66%), 79 (PO_3^+ 11%), 29 ($C_2H_5^+$ 14%).

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