

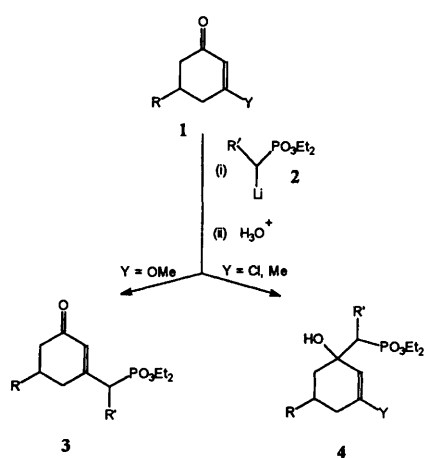
Reaction of phosphorus-stabilized carbanions with cyclic enones. Aromatization of the substitution and addition products

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α -Lithiated alkylphosphonic esters react with substituted cyclohex-2-enones either at the carbonyl group (addition yielding 2-hydroxyalkylphosphonic products) or at the β -carbon (addition-elimination yielding δ -keto phosphonates). Both types of products undergo smooth aromatization when treated with I_2 in MeOH or with pyridinium perbromide in AcOH leading to a variety of benzylphosphonic esters substituted in the aromatic ring with the methoxy or hydroxy groups. Mechanisms of the aromatization reactions are discussed.

Although the Wadsworth–Emmons reaction of cinnamaldehydes has been suggested as a route to 1-aryl-1,3-dienes,¹ phosphorus-stabilized carbanions do not feature at all in recent reviews on the role of the addition to cycloalkenones in organic synthesis.² With the α,β -unsaturated carbonyl compounds, the addition of P-stabilized carbanions can follow the 1,2-, as well as the 1,4- pattern, the regioselectivity varying with the structure of substrates and the reaction conditions.³ We have demonstrated that for cyclohexenones bearing a β -leaving group the reaction can occur at the β -carbon (substitution) or at the carbonyl group (addition) depending on the nature of the β -substituent.⁴ We have now shown that a methyl group substituted at carbon-3 of cyclohexenone directs the lithiated phosphonate exclusively to the carbonyl carbon. These reactions allowed us to prepare a series of 3-(phosphonoalkyl)cyclohex-2-enones (**3**) and 3-substituted 1-(phosphonoalkyl)cyclohex-2-enols (**4**) (Scheme 1).



Scheme 1

In this paper we report the aromatization of products **3** and **4** using methods described in the literature for similar, but non-phosphorus substrates; the aim of the work was to establish a general route to hitherto unknown substituted benzylphosphonates and to shed some light on the mechanism of the oxidative aromatization of cyclohexenone and cyclohexenol derivatives.

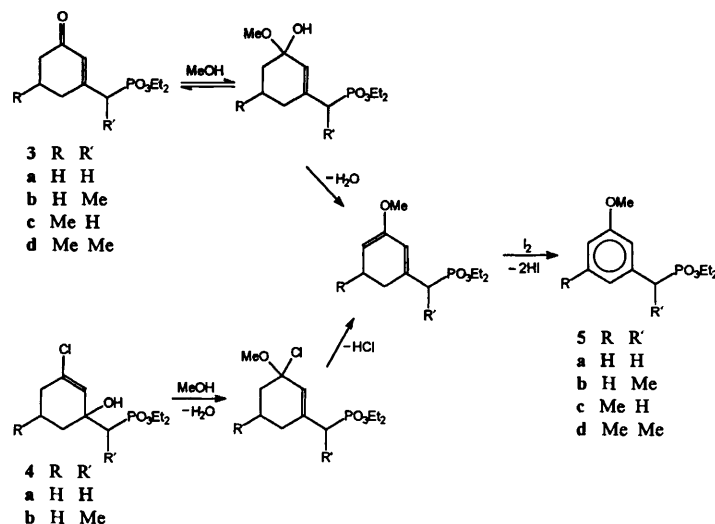
Results and discussion

Metal salt-catalysed aromatization of substituted cyclohexenones to the corresponding phenols or phenol ethers is a well-established procedure.⁵ In 1980 Tamura and Yoshimoto

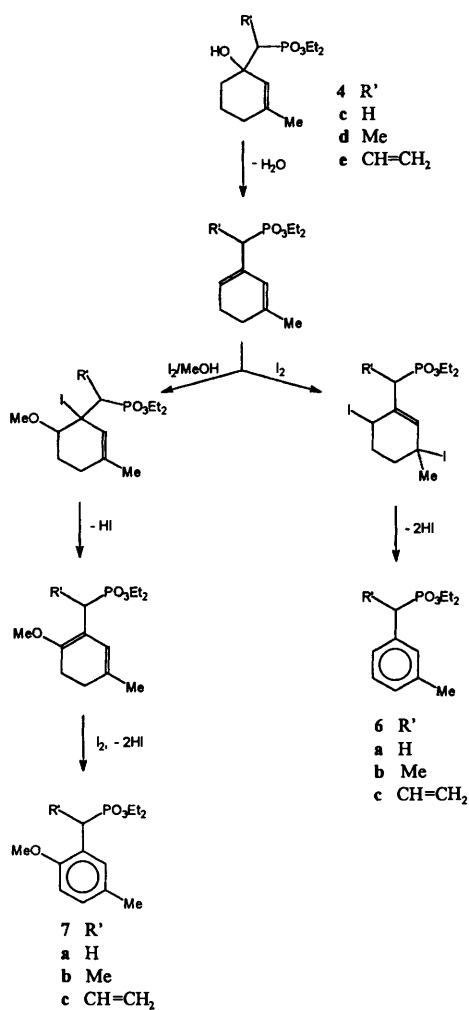
reported aromatization of cyclohexenones using iodine in refluxing methanol.⁶ The approach was recently applied by Kotnis⁷ for the preparation of substituted resorcinols and methoxybenzoates; the only mechanistic suggestion was that the 1,4-addition-elimination of methanol to the enol form of the cyclohexadiene system takes place as a first step of the reaction.

We have subjected some diethyl phosphonic esters **3** and **4** to reaction with I_2 -MeOH and found that the type of aromatic product obtained depends on the structure of the substrate. δ -Keto phosphonates **3** yielded the corresponding (3-methoxybenzyl)phosphonates **5**; we interpret this result as a consequence of an initial 1,2- (independent of the 1,4-) addition of methanol, followed by dehydration and oxidative aromatization (Scheme 2). The same products (**5a** and **5b**) were obtained from the corresponding 3-chlorocyclohexenols (**4a** and **4b**), presumably *via* the acid-catalysed S_N2' displacement of the allylic alcohol by methanol. Elimination of HCl yields the same cyclohexadiene derivative as obtained from **3**, and is followed by the iodine-promoted aromatization. 3-Methyl substituted cyclohexenols (**4**, Y = Me) reacted with iodine in methanol giving two types of aromatic products: the expected 3-methylbenzylphosphonates **6** as well as their 6-methoxy derivatives **7** (Scheme 3). In the latter products the location of the methoxy substituent at carbon-6 of the initial 3-methylcyclohex-2-enol skeleton was unambiguously determined by NMR spectroscopy, including NOE experiments. For example, an NOE experiment carried out for **7a** gave the following results. Irradiation of ring 3-H (5-H in **4**) resulted in an NOE effect at the methoxy methyl (and *vice versa*); irradiation of the 5-Me group led to an NOE effect at the aromatic 4-H and 6-H protons, but not at the OMe group. We propose that both types of products (**6** and **7**) are derived from a common cyclohexadiene intermediate *via* the 1,4-iodine adduct, and the 1,2-solvent incorporated adduct of the diene system, respectively, followed by the usual aromatization steps (Scheme 3). It should be noted that as far as the 1,4-addition to the diene intermediate is concerned, solvent incorporated product would require subsequent elimination of methanol for the aromatization to occur.

It is the 1,4-adduct of iodine which can undergo smooth elimination to the final product **6**. With the 1,2-addition the situation is more complex, as it can, in principle, involve the 6,1 or the 2,3 olefinic bond of the intermediate; each direction yielding a vicinal diiodide or the Markovnikov (M), as well as the anti-Markovnikov (a-M), solvent incorporated products. The observed product **7** results from the a-M addition of I^+ -MeO⁻ species to the 6,1 bond; the I_2 adduct or the M solvent incorporated adduct would lead (after the elimination of HI or MeOH, respectively) to the final 6-iodo substituted analogue of



Scheme 2

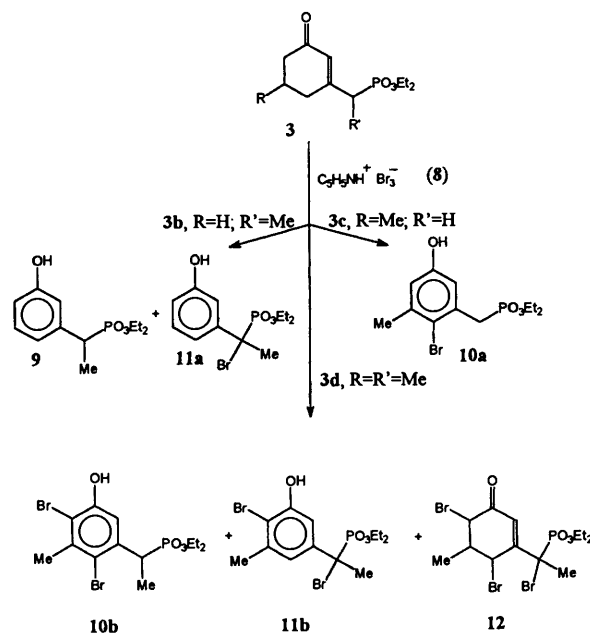


Scheme 3

7. The a-M orientation of the I⁺-MeO⁻ addition can be easily explained by the difference in the substituents present at C-1 and C-6; up to 100% of the a-M selectivity has been observed in the addition of ICl and IBr to unsymmetrically substituted alkenes.⁸ If a bridged iodonium ion structure for the cationic intermediate of the addition to the C₆-C₁ double bond is accepted,⁹ nucleophilic attack of methanol would be expected to occur at the less hindered carbon-6 centre. The absence of the 6-iodo substituted product results probably from the known reversibility of the addition of I₂ to alkenes, increasing the

proportion of the solvent incorporated product containing one strong carbon-oxygen bond. The absence of the aromatic products derived from the 1,2-addition to the C₂-C₃ double bond of the diene intermediate most likely reflects the reluctance of the formation of the sterically more congested 1,2,3-trisubstituted benzene derivative.

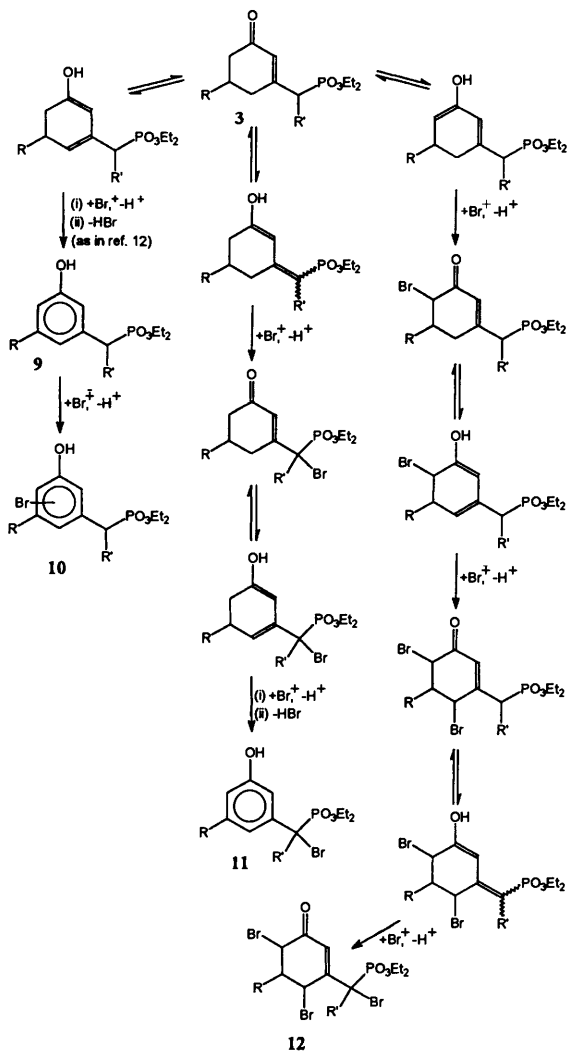
In the second part of this work we have studied the preparation of benzene derivatives by treating 3-(phosphonoalkyl)cyclohexenones **3** with a brominating agent, pyridinium perbromide (**8**). The reagent, easily prepared from pyridine, Br₂ and 48% HBr,¹⁰ was found to be a convenient brominating agent for phenols, alkenes and ketones.¹¹ Meyer and co-workers, in their work on the total synthesis of diterpenoids, found that when a perhydrophenanthrene derivative containing ring C in an enone form was treated with **8**, the ring was converted to a phenolic system fused in the 3,4-positions with the remaining perhydronaphthalene ring. The authors suggested that the reaction involves bromination of the enolic form of the enone system at carbon-2 or carbon-4, followed by the elimination of HBr leading to the phenolic product. When three different substrates of **3** were treated with **8** under conditions reported for the diterpenoid systems,¹² various products were formed depending on the structure of the starting enone. The products, shown in Scheme 4, were separated by



Scheme 4

column chromatography and their structure was unambiguously determined by NMR (^1H , ^{13}C , ^{31}P) and IR spectroscopy, mass spectrometry and elemental analysis. The reaction products can be divided into four categories: phenols (**9**), ring brominated phenols (**10**), α -C side-chain brominated phenols (**11**), and the brominated, but not aromatized substrate **3** (**12**).

In our opinion, the isolation and identification of the products **9–12** sheds more light on the mechanism and the scope of the reaction between cyclic enones and halogenating agents. We propose a general mechanism for the reaction of substrates **3** with reagent **8** (incorporating the original Meyer's mechanism¹² applicable to the formation of **9**) which accounts for all compounds observed in this work (Scheme 5).



It seems that the diversity of the reaction products is a direct function of the availability of the enolizable hydrogens in the substrate. It also seems that fine tuning of the conditions for the reaction system given in Scheme 5 should lead to specific methods of converting ring substituted cyclohexenones into such classes of compounds as substituted phenols, halophenols (when an excess of the halogenating agent is used), or α -haloalkyl derivatives of phenol. The synthetic scope and applications of the aromatization reactions described in this paper are currently under investigation in our laboratory.

Experimental

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 CCl_4 . NMR spectra were recorded on a Bruker AC 300 spectrometer for solutions in CDCl_3 , and the chemical-shift values are given relative to the solvent (^1H , 7.24 ppm; ^{13}C , 77.0 ppm). ^{31}P NMR chemical-shift values are given relative to 85% H_3PO_4 as external standard. When necessary, both ^1H -decoupled and ^1H -coupled ^{13}C NMR spectra were obtained for structural assignments. Heteronuclear proton-carbon correlation spectra were obtained with a relaxation time of 1.5 s between scans, 128 values of t , zero filling to 256 points in f_1 (^1H). NOE experiments were performed with a relaxation time of 0.1 s and to 1024 values of t . J Values are given in Hz. Diastereoisomeric nuclei are denoted by superscripts a and b . Elemental analyses (C/H) were carried out at the Chemistry Department, University of Cape Town.

Preparation of starting diethyl phosphonates

Preparation of **3a**, **3b**, **4a** and **4b** was described previously.⁴ Keto phosphonates **3c** and **3d** were prepared from 3-methoxy-5-methylcyclohex-2-en-1-one and α -lithiated diethyl methyl- or ethyl-phosphonate as described for **3a** and **3b**.⁴

Diethyl (3'-oxo-5-methylcyclohex-1-enyl)methylphosphonate

3c. Purified by column chromatography (AcOEt) (75%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1257 (PO) and 1676 (CO); m/z 260 (M^+ , 66%), 259 (97), 203 (68), 189 (73), and 122 (100); δ_{H} 1.05 (3 H, d, J_{CH} 6.1, 5-Me), 1.30 (6 H, t, J_{CH} 7.1, 2 \times Me of POEt), 1.98–2.53 (5 H, m, 4-H₂, 5-H, 6-H₂), 2.72 (2 H, d, J_{HP} 23.6, α -CH₂), 4.09 (4 H, quintet, J_{HP} , J_{HH} 7.2, 2 \times CH₂ of POEt), 5.93 (1 H, d, J_{HP} 4.6, 2-H); δ_{C} 16.3 (d, J_{CP} 6.3, 2 \times Me of POEt), 20.9 (s, 5-Me), 30.8 (s, C-6), 36.2 (d, J_{CP} 135, α -C), 38.8 (s, C-5), 45.2 (s, C-4), 62.3 (s, 2 \times CH₂ of POEt), 129.1 (d, J_{CP} 11, C-2), 155.2 (d, J_{CP} 12, C-1), 199.2 (s, C=O); δ_{P} 24.2 (Calc. for $\text{C}_{12}\text{H}_{21}\text{O}_4\text{P}$: C, 55.38; H, 8.13. Found: C, 55.06; H, 8.42%).

Diethyl 1-(3-oxo-5-methylcyclohex-1-enyl)ethylphosphonate

3d. Purified by column chromatography (AcOEt) (62%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1257 (PO) and 1676 (CO); m/z 274 (M^+ , 12%), 203 (26), 139 (46), 136 (100) and 121 (38); δ_{H} 1.06 (3 H, two d, J_{HH} 6.2, 5-Me), 1.29 (6 H, m, 2 \times Me of POEt), 1.37 (3 H, two dd, J_{HP} 17.8, J_{HH} 7.2, β -Me), 1.99–2.80 (5 H, m, 4-H₂, 5-H, 6-H₂), 4.07 (4 H, m, 2 \times CH₂ of POEt), 5.96 (1 H, d, J_{HP} 2.7, 1-H); δ_{C} 12.8, 13.3 (two d, J_{CP} 6.3, β -Me), 16.3 (d, J_{CP} 5.7, 2 \times Me of POEt), 20.8 (two s, 5-Me), 30.1 (s, C-5), 37.4 (d, J_{CP} 9.4, C-6), 40.2 (two d, J_{CP} 135, α -C), 45.4 (s, C-4), 62.5 (two d, J_{CP} 6.2, 7.7, 2 \times CH₂ of POEt), 127.5 (two d, J_{CP} 11.9, C-2), 161.3 (d, J_{CP} 8.3, C-1), 199.5 (s, C=O); δ_{P} 27.2, 27.3 (Calc. for $\text{C}_{13}\text{H}_{23}\text{O}_4\text{P}$: C, 56.92; H, 8.54. Found: C, 56.65; H, 8.60%).

Reactions of lithiated diethyl alkylphosphonates with 3-methylcyclohex-2-enone (preparation of **4c**, **4d**, and **4e**).

General procedure

Butyllithium (1.6 mol dm^{-3} solution in hexane; 1.1 mol equiv.) was diluted with tetrahydrofuran (THF, 1.2–2.5 cm^3 mmol⁻¹ of BuLi) and to this solution a solution of diethyl alkylphosphonate (1.0 mol equiv.) in THF (0.5–0.9 cm^3 per mmol of phosphonate) was added at -78°C , and the solution was stirred at that temperature for 20–60 min. In case of diethyl prop-2-enylphosphonate (preparation of **4e**) copper(I) iodide (0.55 mol equiv.) was added and the solution was stirred at -78°C for an additional hour. A solution of 3-methylcyclohex-2-enone (0.75 mol equiv. in the preparation of **4e** and 1.2 mol equiv. in the preparation of **4c** and **4d**) in THF (0.75 cm^3 mmol⁻¹) was added and the reaction mixture was stirred at -78°C for 1 h. Saturated aq. NH_4Cl was added and the resulting solution was extracted with diethyl ether (3 \times 3.5 cm^3 per mmol of the phosphonate). The combined extracts were dried (MgSO_4), filtered, and evaporated under reduced pressure. The

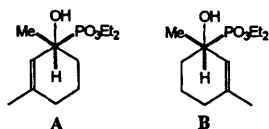


Fig. 1 Relative configuration of chiral centres in two diastereoisomers of **4d**

products were purified and identified as indicated for individual compounds. For **4c**, **4d** and **4e** the assignment of the ^1H NMR signals was additionally confirmed by ^1H - ^{13}C heteronuclear shift correlation experiments.

Diethyl 1-(1-hydroxy-3-methylcyclohex-2-enyl)methylphosphonate 4c. Oil; purified by column chromatography (AcOEt) (42%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1231 (PO) and 3436 (OH); m/z 244 ($\text{M}^+ - \text{H}_2\text{O}$, 49%), 243 (84), 187 (97), 106 (62), 105 (100), 79 (21) and 29 (20); δ_{H} 1.29 (6 H, t, J_{HH} 7.1, 2 \times CH_2 of POEt), 1.54–1.74 (2 H, m, 5- H_2), 1.63 (3 H, s, 3-Me), 1.75–1.92 (4 H, m, 4- H_2 , 6- H_2), 2.01 (1 H, d, J_{HP} 16.3, α - CH^a), 2.04 (1 H, d, J_{HP} 16.3, α - CH^b), 3.82 (1 H, br s, OH), 4.05 (2 H, quintet, J_{HP} , J_{HH} 7.0, CH_2 of POEt a), 4.08 (2 H, quintet, J_{HP} , J_{HH} 7.0, CH_2 of POEt b), 5.43 (1 H, s, 2-H); δ_{C} 15.8 (s, Me of POEt a , J_{CH} 127), 15.9 (s, Me of POEt b , J_{CH} 127), 18.8 (s, C-5, J_{CH} 128), 23.1 (s, 3-Me, J_{CH} 126), 29.3 (s, C-4, J_{CH} 125), 36.1 (d, J_{CP} 8.6, C-6, J_{CH} 128), 37.9 (d, J_{CP} 134, α -C, J_{CH} 130), 61.0 (s, CH_2 of POEt, J_{CH} 147), 67.7 (s, C-1), 126.5 (d, J_{CP} 12, C-2, J_{CH} 157), 136.6 (s, C-3); δ_{P} 30.2 (Calc. for $\text{C}_{12}\text{H}_{23}\text{O}_4\text{P}$: C, 54.95; H, 8.84. Found: C, 54.64; H, 9.05%).

Diethyl 1-(1-hydroxy-3-methylcyclohex-2-enyl)ethylphosphonate 4d. Oil; purified by column chromatography (AcOEt–EtOH, 9:1); two diastereoisomers were obtained. A (25%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1219 (PO) and 3426 (OH); δ_{H} 1.04 (3 H, dd, J_{HP} 17.4, J_{HH} 7.6, β -Me), 1.29 (3 H, t, J_{HH} 7.1, Me of POEt a), 1.30 (3 H, t, J_{HH} 7.1, Me of POEt b), 1.57–1.64 (2 H, m, 5- H_2), 1.66 (3 H, s, 3-Me), 1.73–1.86 (4 H, m, 4- H_2 , 6- H_2), 2.06 (1 H, dq, J_{HP} 19.1, J_{HH} 7.4, α -CH), 4.09 (2 H, quintet, J_{HP} , J_{HH} 7.2, CH_2 of POEt a), 4.10 (2 H, quintet, J_{HP} , J_{HH} 7.2, CH_2 of POEt b), 4.32 (1 H, br s, OH), 5.16 (1 H, s, 2-H); δ_{C} 10.7 (d, J_{CP} 5, β -Me, J_{CH} 133), 15.9 (s, Me of POEt a , J_{CH} 128), 16.0 (s, Me of POEt b , J_{CH} 128), 18.2 (s, C-5, J_{CH} 127), 23.3 (s, C-3, J_{CH} 126), 29.4 (s, C-4, J_{CH} 124), 30.9 (d, J_{CP} 2.9, C-6, J_{CH} 123), 41.7 (d, J_{CP} 133, α -C, J_{CH} 129), 61.1 (s, CH_2 of POEt a , J_{CH} 147), 61.4 (s, CH_2 of POEt b , J_{CH} 147), 70.8 (s, C-1), 125.6 (d, J_{CP} 17.8, C-2, J_{CH} 168), 138.9 (s, C-3); δ_{P} 33.9 (Calc. for $\text{C}_{13}\text{H}_{25}\text{O}_4\text{P}$: C, 56.51; H, 9.12. Found: C, 55.56; H, 9.44%).

B (16%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1219 (PO) and 3426 (OH); δ_{H} 1.13 (3 H, dd, J_{HP} 18.0, J_{HH} 7.3, β -Me), 1.29 (3 H, t, J_{HH} 7.3, Me of POEt a), 1.31 (3 H, t, J_{HH} 7.3, Me of POEt b), 1.58–1.70 (2 H, m, 5- H_2), 1.65 (3 H, s, 3-Me), 1.70–1.85 (4 H, m, 4- H_2 , 6- H_2), 2.05 (1 H, dq, J_{HP} 19.9, J_{HH} 7.5, α -CH), 4.08 (4 H, m, 2 \times CH_2 of POEt), 5.54 (1 H, s, 2-H); δ_{C} 10.6 (d, J_{CP} 4.8, β -Me, J_{CH} 129), 16.3 (s, Me of POEt a , J_{CH} 131), 16.4 (s, Me of POEt b , J_{CH} 131), 19.0 (s, C-5, J_{CH} 133), 23.9 (s, 3-Me, J_{CH} 126), 29.9 (s, C-4, J_{CH} 123), 34.5 (d, J_{CP} 9.8, C-6, J_{CH} 126), 41.7 (d, J_{CP} 133, α -C, J_{CH} 131), 61.5 (s, CH_2 of POEt a , J_{CH} 150), 61.6 (s, CH_2 of POEt b , J_{CH} 150), 70.9 (s, C-1), 124.4 (d, J_{CP} 5.9, C-2, J_{CH} 157), 138.9 (s, C-3); δ_{P} 33.8; m/z (both diastereoisomers) 259 ($\text{M}^+ - \text{H}_2\text{O}$, 17%), 258 (100), 120 (86), 105 (47), 79 (16) and 29 (19).

The relative configuration of the chiral carbons was assigned as α -C(S)/C-1(R) (and its enantiomer) for diastereoisomer A and as α -C(S)/C-1(S) (and its enantiomer) for diastereoisomer B as follows. The most stable conformation of 2-hydroxyalkylphosphonic esters involves *gauche* orientation of the OH and the P=O group, and the *anti* orientation of the C-1 and the C-2 substituents (Fig. 1).¹³ In A, the olefinic hydrogen C-2-H resonates at higher field (δ_{H} 5.16) relative to the C-2-H in B (δ_{H} 5.54) due to the deshielding effect of the *gauche* phosphoryl group in the latter. In addition, the $^3J_{\text{CP}}$ values observed for carbon-2 are large ($J = 17.8$) and small ($J = 5.9$), in agreement with the typical values of $^3J_{\text{CP}} \approx 15$ and $^3J_{\text{CP}} \approx 5$ reported for the *anti* (torsional angle 180°) and the *gauche* (torsional angle 60°) orientations of the P–C–C three bond system.¹⁴

Diethyl 1-(1-hydroxy-3-methylcyclohex-2-enyl)prop-2-enylphosphonate 4e. Oil; purified by column chromatography (AcOEt) (77%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1225 (PO) and 3413 (OH); m/z 270 ($\text{M}^+ - \text{H}_2\text{O}$, 20%), 269 (23), 213 (14), 178 (36), 150 (15), 132 (93), 131 (100), 122 (42), 111 (23), 79 (10), 29 (21); δ_{H} 1.28 (3 H, t, J_{HH} 7.0, Me of POEt a), 1.30 (3 H, t, J_{HH} 7.0, Me of POEt b), 1.57–1.64 (2 H, m, 5- H_2), 1.61 (3 H, s, 3-Me), 1.76–1.82 (4 H, m, 4- H_2 , 6- H_2), 2.73 (1 H, ddt, J_{HP} 19.6, J_{HH} 9.6, 1.5, α -CH), 4.08 (2 H, dq, J_{HP} 7.7, J_{HH} 7.3, CH_2 of POEt a), 4.11 (2 H, dq, J_{HP} 7.7, J_{HH} 7.3, CH_2 of POEt b), 4.25 (1 H, br s, OH), 5.13 (2 H, m, γ - CH_2), 5.26 (1 H, s, 2-H), 5.59 (1 H, m, β -CH); δ_{C} 16.0 (s, Me of POEt a , J_{CH} 125), 16.1 (s, Me of POEt b , J_{CH} 125), 18.3 (s, C-5, J_{CH} 130), 23.4 (s, 3-Me, J_{CH} 126), 29.5 (s, C-4, J_{CH} 123), 32.7 (d, J_{CP} 6.0, C-6, J_{CH} 125), 53.9 (d, J_{CP} 131, α -C, J_{CH} 129), 61.8 (d, J_{CP} 7, CH_2 of POEt a , J_{CH} 152), 62.0 (d, J_{CP} 7, CH_2 of POEt b , J_{CH} 152), 70.3 (d, J_{CP} 3, C-1), 119.8 (d, J_{CP} 13, γ -C, J_{CH} 157), 126.0 (d, J_{CP} 14, C-2, J_{CH} 157), 130.5 (d, J_{CP} 9.5, β -C, J_{CH} 158), 137.9 (s, C-3); δ_{P} 28.8. (Calc. for $\text{C}_{14}\text{H}_{25}\text{O}_4\text{P}$: C, 58.33; H, 8.68. Found: C, 57.78; H, 9.12%).

Reactions of phosphonic esters with iodine in methanol. General procedure

A solution of the phosphonate (1 mol equiv.) and iodine (2 mol equiv.) in methanol (*ca.* 30 cm^3 mmol $^{-1}$ of phosphonate) was heated under reflux in an atmosphere of nitrogen for 90 min. The methanol was evaporated under reduced pressure, the residue was dissolved in benzene and the benzene solution was washed twice with saturated aq. NaHCO_3 , twice with 10% aq. $\text{Na}_2\text{S}_2\text{O}_3$, once with 5% aq. NaOH and twice with water. After drying (MgSO_4) and evaporation of the benzene under reduced pressure, the crude products were purified by column chromatography.

Diethyl (3-methoxyphenyl)methylphosphonate 5a (from 3a). Eluted with AcOEt– CHCl_3 (4:1) (71%); m/z 258 (M^+ , 48%), 230 (9), 202 (12), 148 (71) and 121 (100); δ_{H} 1.23 (6 H, t, J_{HH} 7.1, 2 \times Me of POEt), 3.10 (2 H, d, J_{HP} 21.6, α - CH_2), 3.77 (3 H, s, OMe), 4.00 (4 H, m, 2 \times CH_2 of POEt), 6.75–6.89 (3 H, C-2, C-4, C-6), 7.19 (1 H, dd, J_{HH} 7.7, 7.6, C-5); δ_{C} 16.4 (d, J_{CP} 6, 2 \times Me of POEt), 33.9 (d, J_{CP} 139, α - CH_2), 55.2 (s, OMe), 62.1 (d, J_{CP} 7, 2 \times CH_2 of POEt), 112.6 (s, C-4), 115.4 (d, J_{CP} 6, C-2), 122.2 (d, J_{CP} 6, C-1), 129.4 (s, C-6), 133.8 (s, C-5), 135.8 (s, C-3); δ_{P} 26.9 (Calc. for $\text{C}_{12}\text{H}_{19}\text{O}_4\text{P}$: C, 55.81; H, 7.42. Found: C, 55.38; H, 7.66%).

Diethyl 1-(3-methoxyphenyl)ethylphosphonate 5b (from 3b). Eluted as for **5a** (67%); m/z 272 (M^+ , 82%), 136 (92), and 121 (100); δ_{H} 1.14 (3 H, t, J_{HH} 7.0 Me of POEt a), 1.26 (3 H, t, J_{HH} 7.0, Me of POEt b), 1.55 (3 H, dd, J_{HP} 18.4, J_{HH} 7.6, β -Me), 3.11 (1 H, dq, J_{HP} 22.5, J_{HH} 7.3, α -CH), 3.77 (3 H, s, OMe), 3.77–4.04 (4 H, m, 2 \times CH_2 of POEt), 6.74–6.92 (3 H, 2-H, 4-H, 6-H), 7.20 (1 H, dd, J_{HH} 8.0, 7.8, 5-H); δ_{C} 15.7 (d, J_{CP} 5, 2 \times Me of POEt), 16.4 (two d, J_{CP} 9, 6, β -Me), 38.6 (d, J_{CP} 138, α -C), 55.2 (s, OMe), 62.1 (two d, J_{CP} 7.3, 2 \times CH_2 of POEt), 112.6 (s, C-4), 114.4 (d, J_{CP} 6, C-2), 121.1 (d, J_{CP} 6, C-1), 129.3 (s, C-6), 135.7 (s, C-5), 139.7 (s, C-3); δ_{P} 30.2 (Calc. for $\text{C}_{13}\text{H}_{21}\text{O}_4\text{P}$: C, 57.35; H, 7.77. Found: C, 56.98; H, 7.97%).

Diethyl [(3-methoxy-5-methyl)phenyl]methylphosphonate 5c (from 3c). Oil; eluted as for **5a** (60%); m/z 272 (M^+ , 100%), 162 (55), 149 (43) and 135 (77); δ_{H} 1.24 (6 H, t, J_{HH} 7.1, 2 \times Me of POEt), 2.28 (3 H, s, 5-Me), 3.06 (2 H, d, J_{HP} 21.6, α - CH_2), 3.76 (3 H, s, OMe), 4.00 (4 H, m, 2 \times CH_2 of POEt), 6.59 (1 H, ArH), 6.65 (1 H, ArH), 6.68 (1 H, ArH); δ_{C} 16.4 (d, J_{CP} 6, 2 \times Me of POEt), 21.4 (s, 5-Me), 33.8 (d, J_{CP} 138, α -C), 55.2 (s, OMe), 62.1 (d, J_{CP} 7, 2 \times CH_2 of POEt), 112.4 (s, C-4), 113.5 (d, J_{CP} 6, C-2), 123.1 (d, J_{CP} 7, C-1), 135.7 (s, C-6), 139.2 (s, C-5), 149.7 (s, C-3); δ_{P} 27.1 (Calc. for $\text{C}_{13}\text{H}_{21}\text{O}_4\text{P}$: C, 57.35; H, 7.77. Found: C, 56.68; H, 8.01%).

Diethyl 1-[(3-methoxy-5-methyl)phenyl]ethylphosphonate 5d (from 3d). Oil; eluted as for **5a** (50%); m/z 286 (M^+ , 25%), 176 (50) and 149 (100); δ_{H} 1.15 (3 H, t, J_{HH} 7.1, Me of POEt a), 1.26 (3 H, t, J_{HH} 7.1, Me of POEt b), 1.53 (3 H, dd, J_{HP} 18.4, J_{HH} 7.4, β -

Me), 2.29 (3 H, s, 5-Me), 3.08 (1 H, dq, J_{HP} 15.0, J_{HH} 7.4, α -C), 3.76 (3 H, s, OMe), 3.80–4.07 (4 H, m, 2 \times CH₂ of POEt), 6.58 (1 H, ArH), 6.69 (1 H, ArH), 6.73 (1 H, ArH); δ_C 15.7 (d, J_{CP} 5, 2 \times Me of POEt), 16.4 (d, J_{CP} 5, β -Me), 21.5 (s, 5-Me), 38.5 (d, J_{CP} 138, α -C), 55.1 (s, OMe), 62.1 (two d, J_{CP} 7, 2 \times CH₂ of POEt), 111.4 (s, C-4), 113.4 (d, J_{CP} 3, C-2), 122.0 (d, J_{CP} 7, C-1), 135.7 (s, C-6), 139.2 (s, C-5), 148.9 (s, C-3); δ_P 30.3 (Calc. for C₁₄H₂₃O₄P: C, 58.73; H, 8.11. Found: C, 58.28; H, 8.33%).

Reaction of 4c with I₂-MeOH

Column chromatography (AcOEt) afforded two products.

Diethyl (3-methylphenyl)methylphosphonate 6a. Oil (12%); m/z 242 (M⁺, 40%), 105 (100), 79 (11) and 29 (12); δ_H 1.21 (6 H, t, J_{HH} 7.0, 2 \times Me of POEt), 2.30 (3 H, s, 3-Me), 3.08 (2 H, d, J_{HP} 21.6, α -CH₂), 3.98 (4 H, dq, J_{HP} 7.0, J_{HH} 6.6, 2 \times CH₂ of POEt), 7.04 (3 H, m, 2-H, 4-H, 6-H), 7.18 (1 H, t, J_{HH} 7.4, 5-H); δ_C 16.3 (s, 2 \times Me of POEt, J_{CH} 127), 21.3 (s, 3-Me, J_{CH} 125), 33.7 (d, J_{CP} 138, α -C, J_{CH} 128), 62.8 (s, 2 \times CH₂ of POEt, J_{CH} 145), 126.7 (s, C-4, J_{CH} 159), 126.8 (s, C-5, J_{CH} 159), 127.6 (d, J_{CP} 4, C-6, J_{CH} 158), 128.4 (s, C-2, J_{CH} 159), 130.5 (d, J_{CP} 6, C-1), 138.1 (s, C-3); δ_P 27.3.

Diethyl [(2-methoxy-5-methyl)phenyl]methyl phosphonate 7a. Oil (22%); m/z 272 (M⁺, 100%), 136 (44), 91 (35), 79 (4) and 29 (22); δ_H 1.20 (6 H, t, J_{HH} 7.3, 2 \times Me of POEt), 2.16 (3 H, s, 5-Me), 3.02 (2 H, d, J_{HP} 21.1, α -CH₂), 3.77 (3 H, s, OMe), 3.97 (4 H, quintet, J_{HP} , J_{HH} 7.2, 2 \times CH₂ of POEt), 6.72 (1 H, d, J_{HH} 8.1, C-3), 7.05 (2 H, m, C-4, C-6); δ_C 16.2 (s, 2 \times Me of POEt, J_{CH} 125), 21.1 (s, 5-Me, J_{CH} 127), 32.5 (d, J_{CP} 139, α -C, J_{CH} 127), 55.1 (s, OMe, J_{CH} 143), 61.9 (s, 2 \times CH₂ of POEt, J_{CH} 150), 109.8 (s, C-3, J_{CH} 157), 127.4 (s, C-6, J_{CH} 157), 127.7 (s, C-4, J_{CH} 158), 131.8 (d, J_{CP} 6, C-1), 137.9 (s, C-5), 149.5 (s, C-2); δ_P 27.7.

Reaction of 4d with I₂-MeOH

Column chromatography (AcOEt) afforded only one product in chromatographically pure form.

Diethyl 1-[(2-methoxy-5-methyl)phenyl]ethylphosphonate 7b. Oil (43%); m/z 286 (M⁺, 14%), 149 (100), 134 (8), 119 (15), 79 (3) and 29 (3); δ_H 1.11 (3 H, t, J_{HH} 7.0, Me of POEt^a), 1.25 (3 H, t, J_{HH} 7.0, Me of POEt^b), 1.53 (3 H, dd, J_{HP} 18.5, J_{HH} 7.5, β -Me), 2.31 (3 H, s, 5-Me), 3.10 (1 H, dq, J_{HP} 22.6, J_{HH} 7.5, α -CH), 3.77–3.88 (2 H, m, CH₂ of POEt^a), 3.78 (3 H, s, OMe), 4.00 (2 H, m, CH₂ of POEt^b), 6.74 (1 H, d, J_{HH} 8.2, 3-H), 7.12 (2 H, m, 4-H, 6-H); δ_C 15.6 (d, J_{CP} 16, β -Me, J_{CH} 130), 16.0 (s, Me of POEt^a, J_{CH} 130), 16.3 (s, Me of POEt^b, J_{CH} 130), 21.4 (s, 5-Me, J_{CH} 126), 38.3 (d, J_{CP} 138, α -C, J_{CH} 130), 55.2 (s, OMe, J_{CH} 144), 61.7 (s, CH₂ of POEt^a, J_{CH} 144), 62.3 (s, CH₂ of POEt^b, J_{CH} 144), 109.7 (s, C-3, J_{CH} 156), 127.7 (s, C-6, J_{CH} 160), 128.2 (s, C-4, J_{CH} 159), 135.9 (s, C-5), 137.8 (d, J_{CP} 7, C-1), 149.7 (s, C-2); δ_P 30.3.

Reaction of 4e with I₂-MeOH

Column chromatography (AcOEt) afforded two products.

Diethyl 1-(3-methylphenyl)prop-2-enylphosphonate 6c. Oil (9%); m/z 269 (M⁺ + 1, 84%), 213 (84), 131 (100), 117 (35), 105 (13), 79 (5) and 29 (11); δ_H 1.25 (6 H, t, J_{HH} 7.1, 2 \times Me of POEt), 2.31 (3 H, s, 3-Me), 3.95 (1 H, m, α -CH), 4.04 (quintet, J_{HP} , J_{HH} 6.9, CH₂ of POEt^a), 4.07 (2 H, quintet, J_{HP} , J_{HH} 6.9, CH₂ of POEt^b), 5.21 (2 H, m, γ -CH₂), 6.16 (1 H, m, β -CH), 7.14 (4 H, m, 2-H, 4-H, 5-H, 6-H); δ_C 16.1 (s, Me of POEt^a, J_{CH} 127), 16.2 (s, Me of POEt^b, J_{CH} 127), 21.2 (s, 3-Me, J_{CH} 129), 49.7 (d, J_{CP} 137, α -C, J_{CH} 132), 62.8 (s, CH₂ of POEt^a, J_{CH} 148), 62.9 (s, CH₂ of POEt^b, J_{CH} 148), 118.7 (d, J_{CP} 13, γ -C, J_{CH} 158), 125.8 (s, C-4, J_{CH} 159), 127.9 (s, C-5, J_{CH} 160), 128.4 (s, C-6, J_{CH} 160), 129.5 (s, C-2, J_{CH} 160), 135.1 (s, C-1), 138.1 (s, C-3); δ_P 25.7.

Diethyl 1-[(2-methoxy-5-methyl)phenyl]prop-2-enylphosphonate 7c

Oil (5%); δ_H 1.11 (6 H, t, J_{HH} 7.2, 2 \times Me of POEt), 2.17 (3 H, s, 5-Me), 3.77 (1 H, m, α -CH), 3.78 (3 H, s, OMe), 4.03 (4 H, quintet, J_{HP} , J_{HH} 7.2, 2 \times CH₂ of POEt), 5.21 (2 H, m, γ -CH₂), 6.16 (1 H, m, β -CH), 6.75 (1 H, d, J_{HH} 8.3, 3-H), 7.14 (2 H, m, 4-

H, 6-H); δ_C 16.0 (s, Me of POEt^a, J_{CH} 127), 16.1 (s, Me of POEt^b, J_{CH} 127), 20.7 (s, 5-Me, J_{CH} 129), 48.8 (d, J_{CP} 138, α -C, J_{CH} 133), 55.1 (s, OMe, J_{CH} 144), 62.5 (s, CH₂ of POEt^a, J_{CH} 148), 62.6 (s, CH₂ of POEt^b, J_{CH} 148), 109.9 (s, C-3, J_{CH} 157), 118.5 (d, J_{CP} 14, γ -C, J_{CH} 158), 127.2 (s, C-4, J_{CH} 160), 131.1 (s, C-6, J_{CH} 160), 135.0 (s, C-1), 138.1 (s, C-5), 174.7 (s, C-6); δ_P 26.1.

Reactions of keto phosphonates 3 with pyridinium perbromide.

General procedure

Pyridinium perbromide (1.5 mol equiv.) was added to a solution of 3 (1.0 mol equiv.) in glacial acetic acid (5.3 cm³ mmol⁻¹ of 3) and the solution was stirred at room temperature for 1 h. Water (20 cm³ mmol⁻¹ of 3) was added, the solution was extracted with benzene (3 \times 10 cm³), the combined benzene solution was washed with water (2 \times 10 cm³), dried (Na₂SO₄) and evaporated under reduced pressure. The residue was purified by column chromatography yielding the following pure products.

Reaction of 3b with C₅H₅NH⁺Br₃⁻. Eluted with AcOEt-CHCl₃ (4:1); two products were obtained.

Diethyl 1-bromo-1-(3-hydroxyphenyl)ethylphosphonate 11a. White solid (10%); mp 92 °C; v_{max}/cm^{-1} 3170 (OH); m/z 338, 337, 336 (M⁺, 1.5, 1.1, 1.6%), 257 (100), 201 (89), 200 (13), 198 (14) and 121 (60); δ_H 1.10 (3 H, t, J_{HH} 7.1, Me of POEt^a), 1.33 (t, J_{HH} 7.1, Me of POEt^b), 2.32 (3 H, d, J_{HP} 14.9, β -Me), 3.75 and 3.96 (2 H, two m, CH₂ of POEt^a), 4.22 (2 H, dq, J_{HP} 10.9, J_{HH} 7.1, CH₂ of POEt^b), 6.80 (1 H, d, J_{HH} 7.6, 4-H), 7.06–7.20 (2 H, m, 5-H, 6-H), 7.63 (s, 2-H), 8.4 (1 H, br s, OH); δ_C 16.2 (s, Me of POEt^a), 16.4 (s, Me of POEt^b), 27.5 (d, J_{CP} 16, β -C), 44.6 (d, J_{CP} 138, α -C), 64.9 (two d, J_{CP} 7, 2 \times CH₂ POEt), 116.3 (s, C-4), 117.6 (s, C-6), 118.7 (d, J_{CP} 6, C-2), 128.9 (s, C-5), 139.4 (s, C-1), 156.9 (s, C-3); δ_P 20.8 (Calc. for C₁₂H₁₈BrO₄P: C, 42.75; H, 5.38. Found: C, 43.18; H, 5.43%).

Diethyl 1-(3-hydroxyphenyl)ethylphosphonate 9. Oil (50%); v_{max}/cm^{-1} 3200 (OH); m/z 258 (M⁺, 50%), 230 (9), 201 (14), 121 (100) and 120 (44); δ_H 1.07 (3 H, t, J_{HH} 7.1, Me of POEt^a), 1.29 (3 H, t, J_{HH} 7.1, Me of POEt^b), 1.54 (3 H, dd, J_{HP} 18.8, J_{HH} 7.3, β -Me), 3.11 (1 H, dq, J_{HP} 22.4, J_{HH} 7.5, α -CH), 3.69 and 3.90 (2 H, two m, CH₂ of POEt^a), 4.05 (2 H, dq, J_{HP} 10.9, J_{HH} 7.1, CH₂ of POEt^b), 6.72 (2 H, m, 2-H, 4-H), 7.09–7.15 (2 H, m, 5-H, 6-H), 8.42 (1 H, br s, OH); δ_C 15.7 (d, J_{CP} 5, β -Me), 16.2 (two d, J_{CP} 6, 2 \times Me of POEt), 38.2 (d, J_{CP} 138, α -C), 62.1 (d, J_{CP} 7, CH₂ of POEt^a), 63.2 (d, J_{CP} 7, CH₂ of POEt^b), 114.7 (s, C-4), 115.4 (d, J_{CP} 5, C-2), 120.0 (d, J_{CP} 8, C-6), 129.3 (s, C-5), 138.6 (d, J_{CP} 6, C-1), 157.6 (s, C-3); δ_P 31.0 (Calc. for C₁₂H₁₉O₄P: C, 55.81, H, 7.36. Found: C, 55.28; H, 7.44%).

Reaction of 3c with C₅H₅NH⁺Br₃⁻. Eluted with AcOEt-CHCl₃ (4:1); one product was obtained.

Diethyl [(2-bromo-3-methyl-5-hydroxy)phenyl]methylphosphonate 10a. White solid (50%); mp 108–110 °C; v_{max}/cm^{-1} 3179 (OH); m/z 257 (M⁺ - Br, 54%), 229 (22), 201 (100) and 199 (11); δ_H 1.22 (6 H, t, J_{HH} 7.0, 2 \times Me of POEt), 2.33 (3 H, s, 3-Me), 3.41 (2 H, d, J_{HP} 22.1, α -CH₂), 3.93–4.08 (4 H, m, 2 \times CH₂ of POEt), 6.65 (1 H, d, J_{HH} 2.2, 4-H), 7.06 (1 H, d, J_{HH} 2.2, 6-H), 8.78 (1 H, br s, OH); δ_C 16.2 (d, J_{CP} 6, 2 \times Me of POEt), 24.3 (s, 3-Me), 33.7 (d, J_{CP} 140, α -C), 62.8 (d, J_{CP} 7, 2 \times CH₂ of POEt), 115.9 (d, J_{CP} 5, C-6), 117.5 (s, C-4), 139.7 (s, C-3), 150.1 (s, C-1), 156.1 (s, C-2), 167.7 (s, C-5); δ_P 27.1 (Calc. for C₁₂H₁₈BrO₄P: C, 42.75; H, 5.38. Found: C, 43.10; H, 5.50%).

Reaction of 3d with C₅H₅NH⁺Br₃⁻. Eluted with CHCl₃-AcOEt (3:1); three products were obtained.

Diethyl 1-[(2,4-dibromo-3-methyl-5-hydroxy)phenyl]ethylphosphonate 10b. White solid (4%); mp 160–162 °C; v_{max}/cm^{-1} 3072 (OH); m/z 431, 429 (M⁺, 0.8%, 0.6%), 351 (73), 349 (73), 323 (23), 321 (21), 295 (93), 293 (100), 291 (9), 214 (21) and 212 (16); δ_H 1.05 (3 H, t, J_{HH} 7.0, Me of POEt^a), 1.35 (3 H, t, J_{HH} 7.1, Me of POEt^b), 1.48 (3 H, dd, J_{HP} 18.7, J_{HH} 7.2, β -Me), 2.63 (3 H, s, 3-Me), 3.70 (1 H, dq, J_{HP} 22.5, J_{HH} 7.1, α -CH), 3.86–3.99 (2 H, m, CH₂ of POEt^a), 4.08–4.22 (2 H, m, CH₂ of POEt^b), 7.22 (1 H, d, J_{CP} 3, 6-H), 9.45 (1 H, s, OH); δ_C 16.2 (d, J_{CP} 6, β -C), 16.3 (s,

2 × Me of POEt), 25.4 (s, 3-Me), 36.9 (d, J_{CP} 142, α -C), 62.3 (d, J_{CP} 8, CH₂ of POEt^a), 63.6 (d, J_{CP} 8, CH₂ of POEt^b), 114.1 (s, C-6), (remaining carbons did not yield signals of sufficient intensity); δ_P 30.2 (Calc. for C₁₃H₁₉Br₂O₄P: C, 36.31; H, 4.45. Found: C, 36.79; H, 4.45%).

Diethyl 1-bromo-1-[(3-methyl-4-bromo-5-hydroxy)phenyl]ethylphosphonate 11b. White solid (23%); mp 142–144 °C; ν_{max}/cm^{-1} 3223 (OH); m/z 351, 349 ($M^+ - Br$, 89, 86%), 321 (24), 295 (100), 293 (77), 215 (23), 214 (26), 213 (43) and 212 (23); δ_H 1.17 (3 H, t, J_{HH} 7.0, Me of POEt^a), 1.32 (3 H, t, J_{HH} 7.1, Me of POEt^b), 2.28 (3 H, d, J_{HP} 14.7, β -Me), 2.39 (3 H, s, 3-Me), 3.86, 4.03 (2 H, two m, CH₂ of POEt^a), 4.21 (2 H, dq, J_{HP} 10.8, J_{HH} 7.1, CH₂ of POEt^b), 7.12 (1 H, s, 6-H), 7.18 (1 H, s, 2-H), 7.38 (1 H, br s, OH); δ_C 16.3 (d, J_{CP} 12.7, 2 × Me of POEt), 23.4 (d, J_{CP} 7, β -C), 27.5 (s, 3-Me), 64.7 (d, J_{CP} 7, 2 × CH₂ of POEt), 114.5 (d, J_{CP} 5, C-6), 122.1 (d, J_{CP} 5, C-2), 138.4 (d, J_{CP} 30, C-1), 149.4 (s, C-3), 151.1 (s, C-4), 155.1 (s, C-5); δ_P 20.0 (Calc. for C₁₃H₁₉Br₂O₄P: C, 36.31; H, 4.45. Found: C, 36.80; H, 4.50%).

Diethyl 1-bromo-1-(4,6-dibromo-5-methyl-2-oxocyclohex-1-enyl)ethylphosphonate 12. (Mixture of diastereoisomers). Oil (13%); ν_{max}/cm^{-1} 1152 (PO) and 1695 (CO); m/z 433, 431, 429 ($M^+ - Br$, 62, 80, 77%), 351, 350, 349 ($M^+ - Br - HBr$, 75, 14, 72) and 231 (100); δ_H 1.26–1.37 (6 H, two m, 2 × Me of POEt), 1.41, 1.42 (3 H, two d, J_{HH} 6.2, 6.3, 5-Me), 2.09, 2.10 (3 H, two d, J_{HP} 12.9, β -Me), 2.38 (1 H, m, 5-H), 2.53–2.65 (1 H, m, 6-H), 2.94–3.07 (1 H, m, 4-H), 4.08–4.30 (4 H, m, 2 × CH₂ of POEt), 6.22, 6.25 (1 H, two dd, J_{HH} 2.4, 2.5, 2.5, 2.6, 2-H); δ_C 16.4 (s, 2 × Me of POEt), 18.9 (s, 5-Me), 26.4 (d, J_{CP} 30, β -Me), 36.7, 37.4 (two s, C-5), 46.6, 46.8 (two s, C-4, C-6), 56.0 (d, J_{CP} 120, α -C), 64.5, 65.3 (two d, J_{CP} 7, 2 × CH₂ of POEt), 122.2 (d, J_{CP} 6, C-2), 160.0 (d, J_{CP} 36, C-1), 185.2 (s, CO); δ_P 17.8, 17.9 (Calc. for C₁₃H₂₀Br₃O₄P: C, 30.53; H, 3.94. Found: C, 30.95; H, 4.11%).

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