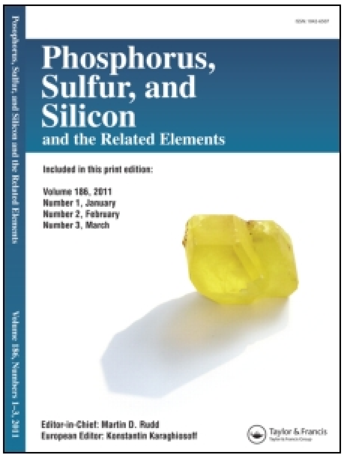

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PHOSPHONIC SYSTEMS. PART 14. REACTIONS OF CYCLOHEXENYLPHOSPHONATES WITH ALDEHYDES

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PHOSPHONIC SYSTEMS. PART 14. REACTIONS OF CYCLOHEXENYLPHOSPHONATES WITH ALDEHYDES

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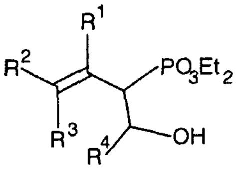
Addition of aldehydes to cyclohexenylphosphonate carbanions could be effected under very mild conditions and generally gave α-addition products. In almost all cases studied, a mixture of diastereoisomers was obtained. As with alkylation,[1] the addition reactions were governed by steric effects.

Key words: Cyclohexenylphosphonic esters; allylic phosphonate carbanions; aldehyde addition; regioselectivity; diastereoisomers.

INTRODUCTION

As demonstrated in a previous paper, cyclohexenylphosphonates can be easily and regiospecifically alkylated.[1] Since the substitution reaction is irreversible, kinetically controlled products were mostly observed. In addition, steric effects were shown to play a significant role in these alkylation reactions. Hence, addition of cyclohexenylphosphonate ester carbanions to carbonyl centres was attempted in order to establish whether the synthetic usefulness of these phosphonates can be extended. A preliminary report was published recently.[2] The resultant 2-hydroxyalkenylphosphonates (**1**) are important precursors of various compounds.[2,3] Due to the planar arrangement of substituents at the electrophilic carbon of aldehydes and ketones, approach of the nucleophile should be facilitated relative to alkyl halides. Moreover, in the former reaction, the addition step is expected to be reversible[2] as shown for prop-2-enylphosphonate (Scheme I), so that thermodynamically controlled products should be observed upon prolonged reaction times.



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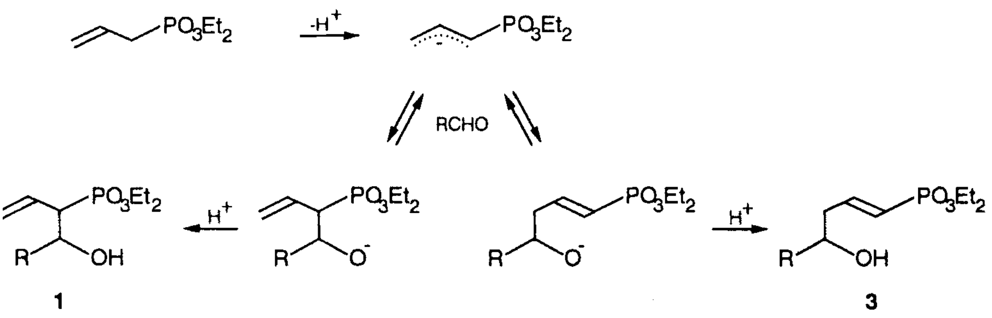
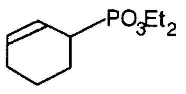


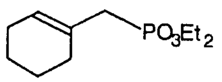
SCHEME I

RESULTS AND DISCUSSION

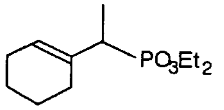
Diethyl cyclohexen-2-ylphosphonate (**2a**) was used as the first model compound while butyllithium was used as base. In most cases studied, addition to aldehydes occurred at the α-position with respect to phosphorus, similar to the reactions with alkyl halides (Scheme II). Products **1** were always obtained as a mixture of two diastereoisomers, usually formed in comparable proportions, although it was possible to vary the ratio somewhat by the rate of addition of the aldehyde to the phosphonate carbanion. Since one of the two chiral carbon atoms (C_α) carries no hydrogen, ^1H n.m.r. spectroscopy could not be used to determine the relative stereochemistry of the diastereoisomers. No other attempts were made to distinguish between the two stereoisomers. Results of the addition reactions are summarised in Table I.



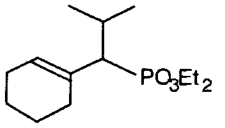
2a



2b



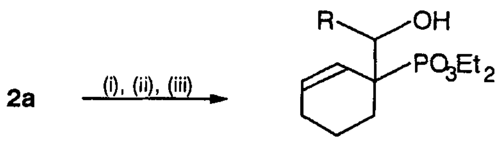
2c



2d

Acetaldehyde was chosen as first electrophile due to the relatively low steric bulk on the carbonyl centre, so the approach of the lithiated anion should be relatively unhindered. The yield of 2-hydroxyphosphonate (**1a**) was nearly quantitative and the reaction occurred exclusively at the α-position with respect to phosphorus. In order to investigate the effect of size of substituents on the carbonyl moiety, other alkanals were used as electrophiles. For propionaldehyde and butyraldehyde, albeit in slightly lower yield than for acetaldehyde, reaction at the α-position proceeded to a very high extent (**1b**, **1c**). This demonstrated that increased chain length of the alkyl substituent of the electrophilic centre does not significantly affect the approach, and subsequent binding, of the nucleophile.

Branching of the side chain on the aldehyde was found to have a dramatic effect on the reaction as was evident from the significantly decreased yield of adduct obtained from the reaction of diethyl cyclohexen-2-ylphosphonate (**2a**) and 2-methylpropionaldehyde. Moreover, in this case, α-addition product was not observed. Addition via the γ-carbon atom of **2a**, accompanied by migration of the double



1a-c; e-i

(i) BuLi, -78°C, THF
(ii) RCHO, -78°C
(iii) aq. NH$_4$Cl

SCHEME II

TABLE I
Addition of phosphonate **2a** to aldehydes

Aldehyde	Product	Yield of product (%) (isolated)	a
acetaldehyde	**1a**	90	99
propionaldehyde	**1b**	65	90
butyraldehyde	**1c**	80	90
2-methylpropionaldehyde	**3a**	40	50
cyclohexylcarboxaldehyde	**1e**	0[b]	0[b]
benzaldehyde	**1f**	48	60
phenylacetaldehyde	**1g**	69	95
3,4,5-trimethoxybenzaldehyde	**1h**	39	60
acrolein	**1i**	71	85

a - yield based upon ^{31}P n.m.r. spectra
b - only non-phosphorus containing products were isolated

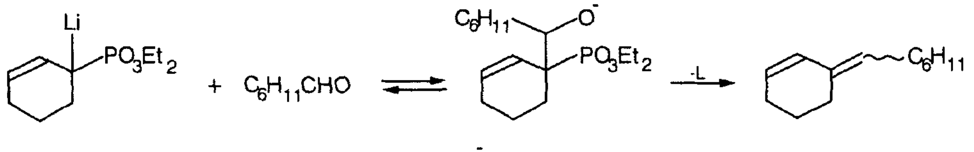
bond, was found to occur yielding the corresponding regioisomer **3a** (see Scheme I). The material balance of the product also included the parent phosphonate **2a** and its isomer (α, β-unsaturated phosphonate). The product **3** could have been formed by direct γ-addition, but more likely the α-adduct was initially formed followed by isomerization (via reversibility of the addition step) to the thermodynamically more stable **3**. Reaction with 2-methylpropionaldehyde, therefore, represents the first example in which steric effects of the chosen substrate are responsible for a total change in the regioselectivity of the condensation process.

Cyclohexylcarboxaldehyde was subsequently used as an analogue of 2-methylpropionaldehyde with increased bulkiness at the tertiary C-2 atom. Although a decreased yield of a corresponding 2-hydroxy adduct **1** was expected, it came as a surprise when it was found that, after work-up of the reaction product, the organic layer contained unreacted **2a** as the only phosphorus-containing compound. In addition, considerable amounts (34%) of E- and Z-3-(cyclohexylmethylidene)cyclohexene were obtained. The diene products could only be formed as a result of the fragmentation of an intermediate α-adduct (**1e**), yielding a diene and lithium diethyl phosphate, the latter being removed upon aqueous work-up (Scheme III). It is evident, however, that the anion of the corresponding 2-hydroxy-phosphonate is unstable in this case, probably as a result of repulsion involving the dialkoxy-phosphoryl group and two carbocyclic substituents.

The hypothesis of steric effects was further tested by the addition of benzaldehyde to a mixture of cyclohexen-2-ylphosphonate and butyllithium in THF. The corresponding 2-hydroxyphosphonate (**1f**) was obtained in good yield. It is thought possible that, due to the planar geometry of the ring on the carbonyl centre of benzaldehyde, approach of the nucleophile is facilitated relative to the non-planar cyclohexyl group in cyclohexylcarboxaldehyde. Insertion of a methylene moiety between the aromatic ring and carbonyl group caused a significant enhancement in adduct formation (**1g**), in agreement with the known fact that the steric bulk of a phenyl ring is greater than that of a benzyl group.[4] Addition to phenylacetaldehyde proceeded to a similar extent than to the less bulky propionaldehyde. Hence, it can be concluded from results of aldehyde addition reactions that steric effects play a dominant role in determining the reactivity of aldehydes towards cyclohexenylphosphonate ester carbanions.

In order to establish the importance of electronic factors on the addition reaction, 3,4,5-trimethoxybenzaldehyde was used as electrophile. Since three electronegative substituents are present on the aromatic ring and only one is capable of conjugation with the aldehyde group, this aldehyde would be expected to be more electrophilic than benzaldehyde. Consequently, it should be more reactive than benzaldehyde under the reaction conditions. However, reaction of the methoxy-substituted aldehyde with diethyl cyclohexen-2-ylphosphonate afforded adduct (**1h**) in comparable yield to benzaldehyde. Thus, it seems as though electronic effects on the aldehyde are less important than steric factors.

The last aldehyde used in the addition reactions of **2a** was acrolein, the simplest acceptor for which regioselectivity of the addition (1,2 vs 1,4) could be tested. The direction of addition should provide some information about the nature of the lithiated **2a**, since increased "hardness" of the nucleophile would lead to 1,2-addition at the carbonyl centre of an α,β-unsaturated aldehyde ("harder" centre[5]), while "softer" nucleophiles would favour a 1,4 fashion of addition. Upon treatment of diethyl cyclohexen-2-ylphosphonate with butyllithium and addition of acrolein, **1i** was found to be the predominant product. No 1,4-addition product was observed,



L = $(EtO)_2PO_2^-$

SCHEME III

even though the terminal end of the double bond is sterically less crowded. The result also demonstrated that addition of the phosphonate carbanion to acrolein is a facile process, since the latter reaction proceeded at a higher rate than polymerisation of the electrophile, which is known to occur easily. The resultant adduct can also polymerise, similar to the adduct of diethyl propen-2-ylphosphonate to acrolein.[6] However, probably due to the bulk of the 2-hydroxycyclohexenylphosphonate, this was not observed and the adduct could be isolated.

In order to extend the investigation of aldehyde addition reactions, diethyl cyclohexen-1-ylmethylphosphonate (**2b**) was used as substrate. Addition to carbonyl centres was expected to be facilitated relative to the cyclohexen-2-ylphosphonate (**2a**) and α-addition, with respect to phosphorus, was expected to predominate. Indeed, diethyl cyclohexen-1-ylmethylphosphonate could be added to various aldehydes. Addition always occurred in the α-position and, as with cyclohexen-2-ylphosphonate, two diastereoisomers were usually obtained. In contrast to adducts of cyclohexen-2-ylphosphonates, products derived from diethyl cyclohexen-1-ylmethylphosphonate contained a structural probe to establish the relative configuration of the stereoisomers. Using the vicinal coupling constants between the hydrogen atoms α to phosphorus and α with respect to the hydroxyl group, structural assignments were made possible. In the proton n.m.r. spectrum, a large coupling constant ($\approx$10 Hz) between these two protons was observed for one isomer. This isomer always resonated at a lower field strength in the ^{31}P n.m.r. spectrum than the isomer with the smaller coupling constant ($\approx$4 Hz) between the two protons under discussion. Since intramolecular attraction between the phosphoryl and hydroxyl group is known,[7] it follows from inspection of the Newman projections of the most populated conformer that the isomer with the larger coupling constant (anti orientation of the vicinal hydrogen atoms) corresponds to the RR or SS pair of enantiomers (Figure 1). By default, the other isomer was denoted as the RS or SR enantiomeric pair. A detailed X-ray and nuclear magnetic resonance spectroscopic investigation into the geometry of these compounds confirmed these assignments.[8] Results of the addition reactions of diethyl cyclohexen-1-ylmethylphosphonate (**2b**) to aldehydes are shown in Scheme IV and summarised in Table II.

Propionaldehyde was demonstrated to add to diethyl cyclohexen-1-ylmethylphosphonate to afford the adduct (**1j**) in a nearly quantitative yield. Steric bulk of substituents on the carbonyl centre of the electrophile was shown to have a lesser effect on the addition step relative to cyclohexen-2-ylphosphonate. This was evident from an experiment in which 2-methylpropionaldehyde added to the phosphonate carbanion to afford the α-substituted product (**1k**), contrary to the reaction of the same aldehyde with diethyl cyclohexen-2-ylphosphonate (**2a**). In addition, reaction

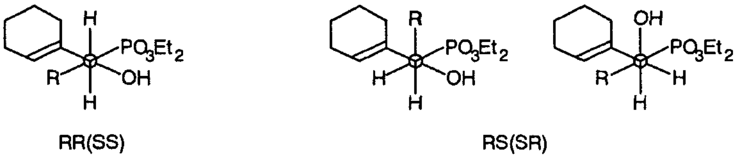
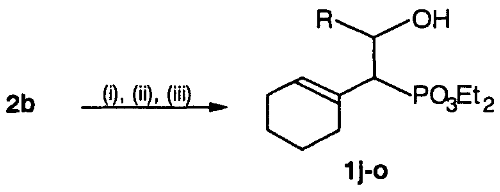


FIGURE 1 Newman projections of diastereomeric adducts of **2b** to aldehydes.



(i) BuLi, -78°C, THF
(ii) RCHO, -78°C
(iii) aq. NH$_4$Cl

SCHEME IV

TABLE II
Addition of phosphonate **2b** to aldehydes

Aldehyde	Product	Yield of product (%) (isolated)	a
propionaldehyde	**1j**	85	95
2-methylpropionaldehyde	**1k**	56	75
cyclohexylcarboxaldehyde	**1l**	43	70
phenylacetaldehyde	**1m**	84	95
benzaldehyde	**1n**	85	90
acrolein	**1o**	78	90

a - yield based upon ^{31}P n.m.r. spectra

of diethyl cyclohexen-1-ylmethylphosphonate and cyclohexylcarboxaldehyde occurred and, this time, resulted in the formation of the α-substituted phosphonate adduct (**1l**) which was stable enough to be isolated. However, only one diastereoisomer (the RS, SR enantiomeric pair) was obtained, which again indicates that steric requirements govern the nucleophilic addition reactions of this aldehyde. Figure 2 represents the approach of the carbanion of **2b** to an aldehyde that should be most favourable from the point of the initial non-bonded interactions between all groups at both trigonal centres. Such stereochemistry of addition leads to the RS(SR) diastereoisomer of the adduct which is, in fact, observed as the exclusive product in the reaction of cyclohexylcarboxaldehyde (Figure 2, R = C_6H_{11}). Examination of the Newman projections shown in Figure 1 indicates, on the other hand, that the RR(SS) diastereoisomer should be the more stable one, because of its ability to minimise the non-bonded interactions about the C_1—C_2 bond. The exclusive formation of the RS(SR) stereoisomer of **1l** suggests an early transition state for the addition, with little bond formation taking place.

As in the case of **2a**, phenylacetaldehyde reacted with **2b** to afford the 2-hydroxy adduct (**1m**) in high yield. Benzaldehyde also gave the expected product (**1n**) in higher yield than that obtained from the reaction of benzaldehyde and cyclohexen-

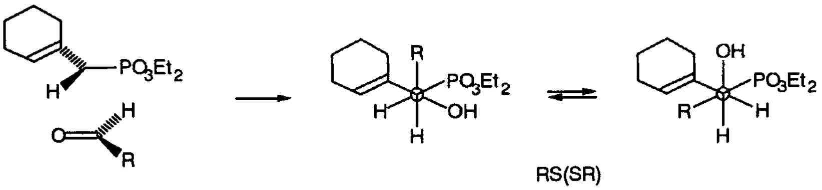


FIGURE 2 Preferred steric course of the addition of **2b** to aldehydes.

TABLE III

Addition of lithiated **2c** and **2d** to aldehydes

Phosphonate	Aldehyde	Product	Yield of product (%) (isolated)	a
2c	benzaldehyde	**1p**	55	70
2d	propionaldehyde	**3b**	30	60
2d	propionaldehyde	**1q**	70[b]	85[b]

a - yield based upon ^{31}P n.m.r. spectra
b - work-up carried out at low temperature

2-ylphosphonate (**2f**). This result again indicates the enhancement in reactivity when the nucleophilic centre is less crowded. Diethyl cyclohexen-1-ylmethylphosphonate was demonstrated to add to acrolein in a regiospecific fashion to give the adduct (**1o**). The carbon *α* with respect to phosphorus acted as the nucleophilic centre and addition took place at the carbonyl carbon of the aldehyde. No 1,4-addition products were observed and polymerisation of the electrophile did not compete.

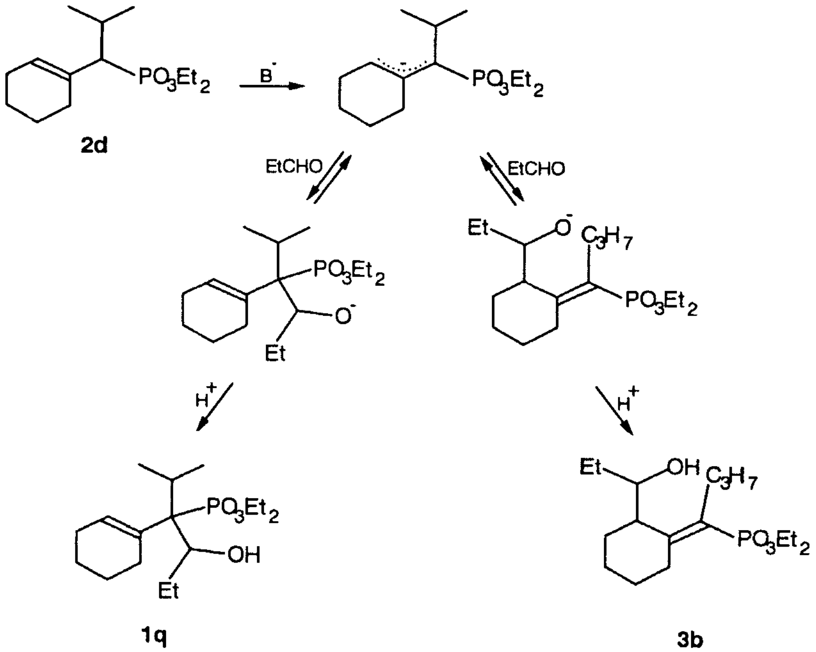
Since diethyl cyclohexen-2-ylphosphonate (**2a**) reacted with alkyl halides[1] and aldehydes to afford a product containing a quaternary carbon atom, *α* with respect to phosphorus, *α*,*α*-disubstituted cyclohexen-1-ylmethylphosphonate derivatives (**2c**, **2d**) were prepared and used as substrates. These phosphonates were expected to react more rapidly with aldehydes after proton abstraction since the *α*-position should be more electron rich. From the facile addition of cyclohexen-2-ylphosphonate (**2a**) to various aldehydes, additional crowding at the *α*-carbon in the cyclohexen-1-ylmethyl analogue (**2c**) was expected to be unimportant as long as similar aldehydes were used. Results of the condensation reactions are summarised in Table III.

Upon treatment of the *α*-methyl substituted phosphonate (**2c**) with base and subsequent addition of benzaldehyde, a fully *α*-substituted hydroxyphosphonate (**1p**) resulted. Although the yield of adduct was somewhat lower than that of the *α*-disubstituted phosphonate (**1n**), the two diastereoisomers resulting from this reaction were isolated in comparable amounts. In addition, the yield of adduct was greater than that obtained from the reaction of cyclohexen-2-ylphosphonate and benzaldehyde (product **1f**).

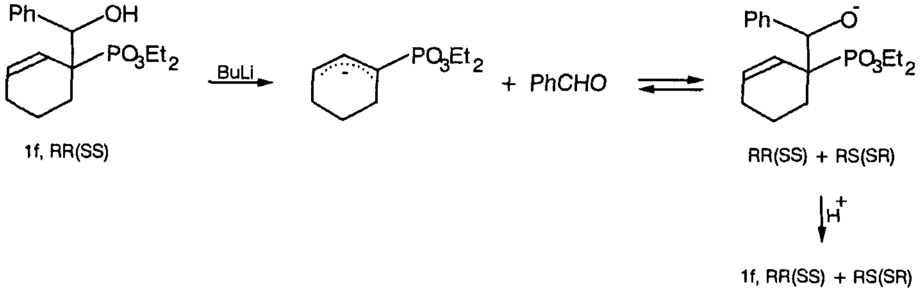
In order to establish the importance of steric congestion versus enhanced nucleophilicity of the *α*-carbon, the *α*-iso-propyl substituted carbanion, derived from **2d**, was treated with propionaldehyde. Usual work-up of the reaction mixture at ambient temperature afforded γ-substituted product (**3b**) as the major component of the reaction mixture. However, quenching of the reaction mixture with aqueous ammonium chloride solution at low temperature afforded the α-substituted product (**1q**). This clearly indicates that α-addition is the kinetic pathway and that it is a reversible process. At elevated temperatures, isomerisation of the olefinic bond and subsequent recombination occurs to give the thermodynamic γ-substituted adduct. The latter step is also reversible, as demonstrated by the observation that parent phosphonate (**2d**) was recovered upon treatment of the γ-adduct with base. The reaction of **2d** with propionaldehyde is shown in Scheme V.

Reversibility of the condensation step for similar type of reactions is well established.[9] However, although the presence of parent phosphonate gave an indication of reversibility when these adducts were treated with base, recombination should also occur. Hence, the diastereomeric mixture of adducts of diethyl cyclohexen-2-ylphosphonate and benzaldehyde (product **1f**) was separated to individual stereoisomers. Treatment of the RR(SS) enantiomeric pair with butyllithium resulted in the decomposition of the adduct to parent phosphonate. Since the resultant phosphonate carbanion can be approached again by the aldehyde in any spatial orientation, recombination should result in a mixture of diastereoisomers. This was, indeed, observed. Even though a single diastereoisomer was used initially, comparable amounts of both RR(SS) and RS(SR) diastereoisomers were recovered (Scheme VI).

Dialkyl 2-hydroxyalkenylphosphonates are important precursors of dienes.[10] Their fragmentation usually occurs under mild conditions which is an advantage over the Wittig procedure[11] for diene formation. In this study, a number of new 2-hydrox-



SCHEME V



1f, RR(SS)

RR(SS) + RS(SR)

1f, RR(SS) + RS(SR)

SCHEME VI

yalkenyl-phosphonates were prepared under very mild conditions. The effects of steric bulk on both the nucleophilic and the electrophilic sites in the condensations leading to those systems were investigated. It was demonstrated that the rate, as well as the regioselectivity of the reaction were influenced by steric factors. In some cases, either thermodynamic or kinetic products could be isolated, depending on the work-up procedure. The fragmentation of these phosphonates to dienes will be the topic of a following paper.

EXPERIMENTAL

All compounds prepared, were fully characterised by high resolution (300 MHz)^{1}H, ^{13}C and ^{31}P n.m.r., as well as infrared spectroscopy and mass spectrometry. Spectral and analytical data are reported in the individual syntheses. The preparation of phosphonates **2a–d** was described in previous papers.[1,12]

General procedure for addition reactions. The phosphonate (5 mmol) in dry THF (10 ml), under an inert atmosphere, was cooled to −78°C whereupon a 1,6 M solution of butyllithium (8.5 mmol) was added dropwise. After stirring for 1 h, the relevant electrophile (8 mmol) was added slowly and stirring was continued at −78°C for 30 min. The reaction mixture was then allowed to reach ambient temperature and stirred for an additional 16 h. Subsequent washing with aqueous ammonium chloride solution, extraction with methylene chloride, drying and concentration afforded the crude product which was purified by column (Kieselgel 60) or preparative thin layer chromatography (Kieselgel 60 PF_{254}).

(A) Addition to diethyl cyclohexen-2-ylphosphonate (**2a**). The following compounds were prepared:†

(**i**) From acetaldehyde. Two diastereoisomers of diethyl 1-(1′-hydroxyethyl)cyclohexen-2-ylphosphonate (**1a**), purified and separated by chromatography (column; ethyl acetate/hexane; 1:1); (90,0% [99]), as oils, b.p. decomp.; ^{1}H n.m.r. ($CDCl_3$) 1,09 (3H, d, J_{HH} 6.5 Hz) 1,27 (6H, t, J_{HH} 7.1 Hz) 1,68 (2H, m) 1,96 (4H, m) 4,00 (1H, m, J_{HH} 6.5 Hz) 4,07 (4H, quint, $J_{HH} = J_{HP}$ 7.1 Hz) 5,72 (1H, m) 6,05 (1H, m); ^{31}P n.m.r. 31,98; ^{13}C n.m.r. 16,3 (2 × Me, q, J_{CH} 129.6 Hz) 18,9 (CH_2, t, J_{CH} 127.4 Hz) 22,2 (CH_2, t, J_{CH} 129.5 Hz) 23,2 (Me, q, J_{CH} 119.6 Hz) 25,1 (CH_2, t, J_{CH} 119.6 Hz) 45,9 (C_1, d, J_{CP} 133.1 Hz) 62,2 (2 × CH_2, t, J_{CH} 147.8 Hz) 70,5 (CH, d, J_{CH}) 145.9 Hz) 121,9 (CH, d, J_{CH} 159.6 Hz) 133,2 (CH, d, J_{CH} 142.2 Hz) and ^{1}H n.m.r. ($CDCl_3$) 1,14 (3H, d, J_{HH} 6.5 Hz) 1,27 (6H, t, J_{HH} 7.1 Hz) 1,68 (2H, m) 1,96 (4H, m) 3,91 (1H, dq, $J_{HH} = J_{HP}$ 6.5 Hz) 4,07 (4H, quint, $J_{HH} = J_{HP}$ 7.1 Hz) 5,48 (1H, m) 5,93 (1H, m); ^{31}P n.m.r. 32,44; ^{13}C n.m.r. 16,3 (2 × Me, q, J_{CH} 129.6 Hz) 18,9 (CH_2, t, J_{CH} 127.4 Hz) 22,2 (CH_2, t, J_{CH} 129.5 Hz) 23,0 (Me, q, J_{CH} 119.6 Hz) 25,1 (CH_2, t, J_{CH} 119.6 Hz) 45,1 (C_1, d, J_{CP} 133.7 Hz) 62,7 (2 × CH_2, t, J_{CH} 147.8 Hz) 70,5 (CH, d, J_{CH} 145.9 Hz) 124,1 (CH, d, J_{CH} 160.1 Hz) 131,4 (CH, d, J_{CH} 150.0 Hz); MS, m/z 263 (M^+ 2,7%), 218 (100%), 190 (23,3%), 162 (52,1%), 79 (25,5%).

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†All adducts prepared in this work contain a cyclohexene ring and two ethoxy groups of the phosphonate moiety. The hydrogen atoms of these fragments of the molecule give rise to ^{1}H and ^{13}C n.m.r. signals practically identical for each of the compounds listed below. The chemical shifts of these signals will, therefore, only be given for the first product listed (**1a**) and, for brevity's sake, will be omitted in the spectroscopic data given for the remaining adducts.

(ii) From priopionaldehyde. Two diastereoisomers of diethyl 1-(1′-hydroxypropyl)cyclohexen-2-ylphosphonate (**1b**), purified and separated by chromatography (prep t.l.c. ether/hexane; 2:3); (64,9% [90]), as oils; ν_{max} ($CHCl_3$) 3363 cm^{-1}, ^{1}H n.m.r. ($CDCl_3$) 0,95 (3H, t, J_{HH} 7.3 Hz) 1,60 (2H, m) 3,75 (1H, m) 5,70 (1H, m) 5,99 (1H, m); ^{31}P n.m.r. 31,82; ^{13}C n.m.r. 11,3 (Me, q, J_{CH} 122.1 Hz) 24,5 (CH_2, t, J_{CH} 127.0 Hz) 45,9 (C_1, d, J_{CP} 134.8 Hz) 76,5 (CH, d, J_{CH} 147.0 Hz) and ^{1}H n.m.r. ($CDCl_3$) 0,96 (3H, t, J_{HH} 7.3 Hz) 1,60 (2H, m) 3,60 (1H, m) 5,53 (1H, m) 5,94 (1H, m); ^{31}P n.m.r. 32,11; ^{13}C n.m.r. 11,4 (Me, q, J_{CH} 122.1 Hz) 24,6 (CH_2, t, J_{CH} 125.7 Hz) 45,9 (C_1, d, J_{CP} 134.8 Hz) 76,5 (CH, d, J_{CH} 147.0 Hz); MS, m/z 277 (M^+, 5,9%), 260 (2,8%), 247 (6,2%), 218 (100%), 190 (28,3%), 162 (57,0%), 79 (34,8%).

(iii) From butyraldehyde. Two diastereoisomers of diethyl 1-(1′-hydroxybutyl(cyclohexen-2-ylphosphonate (**1c**), purified and separated by chromatography (column; 40% ethyl acetate/hexane); (79,5% [90]), as oils; ^{1}H n.m.r. ($CDCl_3$) 0,85 (3H, t, J_{HH} 6.9 Hz) 1,35 (2H, m) 1,68 (2H, m) 3,66 (1H, m) 5,70 (1H, m) 5,99 (1H, m); ^{31}P n.m.r. 32,07; ^{13}C n.m.r. 13,9 (Me, q, J_{CH} 124.4 Hz) 19,8 (CH_2, t, J_{CH} 126.2 Hz) 34,2 (CH_2, t, J_{CH} 125.7 Hz) 45,1 (C_1, d, J_{CP} 134.2 Hz) 74,5 (CH, d, J_{CH} 144.7 Hz) and ^{1}H n.m.r. ($CDCl_3$) 0,86 (3H, t, J_{HH} 6.9 Hz) 1,35 (2H, m) 1,68 (2H, m) 3,66 (1H, m) 5,51 (1H, m) 5,93 (1H, m); ^{31}P n.m.r. 32,43; ^{13}C n.m.r. 13,9 (Me, q, J_{CH} 124.4 Hz) 19,9 (CH_2, t, J_{CH} 126.2 Hz) 33,8 (CH_2, t, J_{CH} 125.7 Hz) 45,1 (C_1, d, J_{CP} 134.3 Hz) 74,5 (CH, d, J_{CH} 144.7 Hz); MS, m/z 291 (M^+, 4,6%), 247 (6,2%), 218 (100%), 190 (23,4%), 162 (41,7%), 79 (25,7%).

(iv) From benzaldehyde. Two diastereoisomers of diethyl 1-(hydroxyphenylmethyl)-cyclohexen-2-ylphosphonate (**1f**), purified and separated by chromatography (prep. t.l.c.; 50% diethyl ether/hexane); (47,7% [60]) of which one was an oil; ν_{max} ($CHCl_3$) 3399, 1600 cm^{-1}, ^{1}H n.m.r. ($CDCl_3$) 1,05 (1H from cyclohexene ring, m) 4,96 (1H, d, J_{HH} 13.4 Hz) 5,70 (1H, m) 5,81 (1H, m) 7,25 (5H, m); ^{31}P n.m.r. 31,98; ^{13}C n.m.r. 46,3 (C_1, d, J_{CP} 130.8 Hz) 76,2 (CH, d, J_{CH} 147.5 Hz) 127,1 (2 × CH, d, J_{CH} 153.3 Hz) 127,3 (2 × CH, d, J_{CH} 159.9 Hz) 127,7 (CH, d, J_{CH} 157.8 Hz) 139,4 (C, s) and the other, colourless crystals (from hexane) m.p. 84,2-84.4°C; ^{1}H n.m.r. ($CDCl_3$) 0,59 (1H from cyclohexene ring, m) 4,88 (1H, d, J_{HH} 11.6 Hz) 6,05 (2H, s) 7,25 (5H, m); ^{31}P n.m.r. 32,29; ^{13}C n.m.r. 46,1 (C_1, d, J_{CP} 130.7 Hz) 76,9 (CH, d, J_{CH} 146.6 Hz) 127,1 (2 × CH, d, J_{CH} 153.3 Hz) 127,3 (2 × CH, d, J_{CH} 159.9 Hz) 127,7 (CH, d, J_{CH} 157.8 Hz) 139,3 (C, s); MS, m/z 322 (M^+, 8,5%), 280 (52,7), 218 (8,9%), 189 (18,2%), 170 (19,8%), 105 (32,1%), 91 (100%), 79 (48,6%).

(v) From phenylacetaldehyde. Two diastereoisomers of diethyl 1-(1′-hydroxy-2′-phenyl-ethyl)cyclohexen-2-ylphosphonate (**1g**), purified and separated by chromatography (prep. t.l.c.; diethyl ether/hexane; 2:3); (69,0% [95]), as oils; ^{1}H n.m.r. ($CDCl_3$) 3.01 (1H, d, J_{HP} 13.9 Hz), 3,98 (1H, m) 4.03 (1H, m) 5.81 (1H, m) 6,10 (1H, m) 7,22 (5H, m); ^{31}P n.m.r. 31,44; ^{13}C n.m.r. 38,6 (CH_2, t, J_{CH} 127.1 Hz) 45,7 (C_1, d, J_{CP} 136.3 Hz) 76,0 (CH, d, J_{CH} 152.7 Hz) 126,0 (CH, d, J_{CH} 159.1 Hz) 128,1 (2 × CH, d, J_{CH} 160.0 Hz) 129,1 (2 × CH, d, J_{CH} 156.8 Hz) 139,8 (C, s) and ^{1}H n.m.r. ($CDCl_3$) 2,62 (1H, dd, J_{HH} 10.3 Hz, J_{HH} 13.8 Hz) 2,86 (1H, d, J_{HP} 13.8 Hz) 4.02 (1H, m) 5.62 (1H, m) 6,06 (1H, m) 7,21 (5H, m); ^{31}P n.m.r. 31,88; ^{13}C n.m.r. 38,3 (CH_2, t, J_{CH} 127.1 Hz) 45,7 (C_1, d, J_{CP} 136.3 Hz) 76,0 (CH, d, J_{CH} 152.7 Hz) 125,9 (CH, d, J_{CH} 159.1 Hz) 128,0 (2 × CH, d, J_{CH} 160.0 Hz) 129,1 (2 × CH, d, J_{CH} 156.8 Hz) 139,8 (C, s); MS, m/z 247 (17,1%), 218 (100%), 190 (24,7%), 162 (41,9%), 91 (63,6%), 79 (35,7%).

(vi) From 3,4,5-trimethoxybenzaldehyde. Two diastereoisomers of diethyl 1-[(hydroxy)-(3,4,5-trimethoxyphenyl)methyl]cyclohexen-2-ylphosphonate (**1h**), purified and separated by chromatography (column; ethyl acetate); (39,0% [62]), as oils; ν_{max} ($CHCl_3$) 3600, 3490, 1610 cm^{-1}, ^{1}H n.m.r. ($CDCl_3$), 1,06 (1H from cyclohexene ring, m) 3,75 (3H, s) 3,77 (6H, s) 4,87 (1H, d, J_{HH} 12.3 Hz) 5,68 (1H, m) 5,84 (1H, m) 6,52 (2H, s); ^{31}P n.m.r. 31,89 and ^{1}H n.m.r. ($CDCl_3$) 0,68 (1H from cyclohexene ring, m) 3,75 (3H, s) 3,77 (6H, s) 4,73 (1H, d, J_{HH} 11.1 Hz) 6,05 (2H, s) 6,55 (2H, s); ^{31}P n.m.r. 32,24; MS, m/z 414 (M^+, 4,4%), 397 (5,1%), 218 (100%), 190 (25,7%), 162 (37,6%), 79 (24,3%).

(vii) From acrolein. Two diastereoisomers of diethyl 1-(1′-hydroxypropen-2′-yl)cyclohexen-2-ylphosphonate (**1i**), purified and separated by chromatography (prep. t.l.c.; diethyl ether); (70,8% [85]), as oils; ν_{max} ($CHCl_3$) 3395, 1644 cm^{-1}, ^{1}H n.m.r. ($CDCl_3$) 4,12 (1H, m) 5,05 (1H, d, J_{HH} 10.2 Hz) 5,15 (1H, t, J_{HH} 17.5 Hz) 5,66 (1H, m) 5,74 (1H, m) 5,91 (1H, m); ^{31}P n.m.r. 31,29; ^{13}C n.m.r. 44,3 (C_1, d, J_{CP} 137.4 Hz) 76,3 (CH, d, J_{CH} 151.4 Hz) 117.1 (CH_2, t, J_{CH} 155.2 Hz) 135,9 (CH, d, J_{CH} 155.5 Hz) and ^{1}H n.m.r. ($CDCl_3$) 4,34 (1H, m) 5,05 (1H, d, J_{HH} 10.2 Hz) 5,19 (1H, t, J_{HH} 19.0 Hz) 5,50 (1H, m) 5,75 (1H, m) 5,86 (1H, m); ^{31}P n.m.r. 31,47; ^{13}C n.m.r. 44,7 (C_1, d, J_{CP} 137,4 Hz) 74,9 (CH, d, J_{CH} 151.2 Hz) 115,9 (CH_2, t, J_{CH} 156.8 Hz) 135,5 (CH, d, J_{CH} 154.8 Hz); MS, m/z 275 (M^+ 0,6%), 257 (1,2%), 218 (100%), 190 (26,2%), 162 (77,7%), 79 (56,6%).

(viii) From 2-methylpropionaldehyde. Two diastereoisomers of diethyl 3-(1′-hydroxy-2′-methylpropyl)cyclohexen-1-ylphosphonate (**3a**), purified and separated by chromatography (column; ethyl acetate/hexane; 1:1); (39,8% [50]), as oils; ν_{max} ($CHCl_3$) 3336, 1631 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 0,85 (3H, d, J_{HH} 6.8 Hz) 0,87 (3H, d, J_{HH} 6.8 Hz) 1,5-2,3 (8H, m) 3,26 (1H, dd, J_{HH} 6.8 Hz, J_{HH} 5.0 Hz) 6,57 (1H, d,

J_{HH} 21.6 Hz); ^{31}P n.m.r. 20,91; ^{13}C n.m.r. 19,4 (2 × Me, q, J_{CH} 137.6 Hz) 21,0 (CH_2, t, J_{CH} 131.0 Hz) 21,5 (CH_2, t, J_{CH} 131.0 Hz) 24,3 (CH_2, t, J_{CH} 129.5 Hz) 29,9 (CH, d, J_{CH} 125.1 Hz) 39,6 (CH, d, J_{CH} 123.1 Hz) 78,6 (CH, d, J_{CH} 138.5 Hz) 129,5 (C, d, J_{CP} 174.7 Hz) 145,4 (CH, d, J_{CH} 157.4 Hz) and ^{1}H n.m.r. ($CDCl_3$) 0,86 (3H, d, J_{HH} 6.9 Hz) 0,92 (3H, d, J_{HH} 6.9 Hz) 1,5-2,3 (8H, m) 3,08 (1H, dd, J_{HH} = J_{HH} 5.7 Hz) 6,84 (1H, d, J_{HH} 23.6 Hz); ^{31}P n.m.r. 21,20; ^{13}C n.m.r. 19,4 (2 × Me, q, J_{CH} 137.6 Hz) 21,0 (CH_2, t, J_{CH} 131.0 Hz) 24,3 (CH_2, t, J_{CH} 129.5 Hz) 30,6 (CH, d, J_{CH} 125.1 Hz) 39,6 (CH, d, J_{CH} 123.1 Hz) 78,6 (CH, d, J_{CH} 138.5 Hz) 128,6 (C, d, J_{CP} 174.7 Hz) 144,1 (CH, d, J_{CH} 160.5 Hz); MS, m/z 290 (M^+, 9,1%), 275 (18,2%), 218 (100,0%), 190 (16,9%), 178 (83,3%), 162 (24,8%), 138 (30,1%), 79 (31,3%).

(ix) From cyclohexylcarboxaldehyde. Two diastereoisomers of 3-cyclohexylmethylidenecyclohexene, purified and separated by chromatography (column; hexane and ethyl acetate); E-3-cyclohexylmethylidenecyclohexene (19,5%); ^{1}H n.m.r. ($CDCl_3$) 1,29 (6H, m) 1,66 (6H, m) 2,10 (2H, m) 2,20 (1H, m) 2,35 (2H, m) 5,08 (1H, d, J_{HH} 10.0 Hz) 5,63 (1H, dt, J_{HH} 10.0 Hz, J_{HH} 4,2 Hz) 5,98 (1H, dt, J_{HH} 10,0 Hz, J_{HH} 2,0 Hz) and Z-3-cyclohexylmethylidenecyclohexene (13,9%); ^{1}H n.m.r. ($CDCl_3$) 1,29 (6H, m) 1,66 (6H, m) 2,10 (2H, m) 2,15 (1H, m) 2,22 (2H, m) 4,93 (1H, d, J_{HH} 10.0 Hz) 5,77 (1H, ddt, J_{HH} 10.0 Hz, J_{HH} 4.0 Hz, J_{HH} 1.9 Hz) 6,39 (1H, dt, J_{HH} 10.1 Hz, J_{HH} 2.0 Hz).

(B) Addition to diethyl cyclohexen-1-ylmethylphosphonate (**2b**). The following products were prepared:

(i) From propionaldehyde. Two diastereoisomers of diethyl 1-(cyclohexen-1′-yl)-2-hydroxybutylphosphonate (**1j**), purified and separated by chromatography (prep. t.l.c.; diethyl ether/hexane; 2:3); (84,8% [95]), as oils; ν_{max} ($CHCl_3$) 3591, 3421, 1669 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 0,87 (3H, t, J_{HH} 7.3 Hz) 1.57 (2H, m) 2,36 (1H, dd, J_{HH} 4.0 Hz, J_{HP} 24.5 Hz) 3,90 (1H, m) 5,72 (1H, m); ^{31}P n.m.r. 29,50; ^{13}C n.m.r. 9,5 (Me, q, J_{CH} 125.3 Hz) 16,3 (2 × Me, q, J_{CH} 127.1 Hz) 22,0 (CH_2, t, J_{CH} 127.7 Hz) 22,8 (CH_2, t, J_{CH} 127.6 Hz) 25,2 (CH_2, t, J_{CH} 124.3 Hz) 27,8 (CH_2, t, J_{CH} 126.2 Hz) 28,6 (CH_2, t, J_{CH} 125.7 Hz) 52,6 (CH, dd, J_{CH} = J_{CP} 129.6 Hz) 61,9 (CH_2, t, J_{CH} 145.3 Hz) 62,6 (CH_2, t, J_{CH} 145.3 Hz) 71,2 (CH, d, J_{CH} 146.0 Hz) 127,4 (CH, d, J_{CH} 152.7 Hz) 131,4 ($C_{1'}$, s) and ^{1}H n.m.r. ($CDCl_3$) 0,92 (3H, t, J_{HH} 7.3 Hz) 1,57 (2H, m) 2,39 (1H, dd, J_{HH} 9.6 Hz, J_{HP} 20.4 Hz) 3,89 (1H, m) 5,58 (1H, m); ^{31}P n.m.r. 30,35; ^{13}C n.m.r. 10,3 (Me, q, J_{CH} 125.3 Hz) 16,4 (2 × Me, q, J_{CH} 127.1 Hz) 21,9 (CH_2, t, J_{CH} 127.7 Hz) 22,9 (CH_2, t, J_{CH} 127.6 Hz) 25,5 (CH_2, t, J_{CH} 124.3 Hz) 27,7 (CH_2, t, J_{CH} 126.2 Hz) 29,9 (CH_2, t, J_{CH} 125.7 Hz) 51,7 (CH, dd, J_{CH} = J_{CP} 129.6 Hz) 61,5 (CH_2, t, J_{CH} 145.3 Hz) 62,9 (CH_2, t, J_{CH} 145.3 Hz) 71,4 (CH, d, J_{CH} 146.0 Hz) 128,6 (CH, d, J_{CH} 152.7 Hz) 130,0 ($C_{1'}$, s); MS, m/z 291 (M^+, 10,8%), 273 (52,2%), 232 (17,7%), 204 (45,7%), 176 (61,7%), 135 (100%), 94 (58,9%).

(ii) From 2-methylpropionaldehyde. Two diastereoisomers of diethyl 1-(cyclohexen-1′-yl)-2-hydroxy-3-methylbutylphosphonate (**1k**), purified and separated by chromatography (prep. t.l.c.; diethyl ether/hexane; 2:3); (55,3% [75]) of which the RS(SR) stereoisomer was an oil; ^{1}H n.m.r. ($CDCl_3$) 0,81 (3H, d, J_{HH} 6.7 Hz) 0,92 (3H, d, J_{HH} 6.7 Hz) 1,74 (1H, ddq, J_{HH} = J_{HH} = J_{HP} 7.1 Hz) 2,53 (1H, dd, J_{HH} 3.9 Hz, J_{HP} 25.2 Hz) 3,62 (1H, dd, J_{HH} 4.3 Hz, J_{HH} 6.5 Hz) 5,74 (1H, m); ^{31}P n.m.r. 29,95 and the RR(SS) stereoisomer colourless crystals, m.p. (from hexane) 97,0–97,2°C; ^{1}H n.m.r. ($CDCl_3$) 0,77 (3H, d, J_{HH} 6.7 Hz) 0,93 (3H, d, J_{HH} 6.7 Hz) 1,71 (1H, ddq, J_{HH} = J_{HH} 2.2 Hz, J_{HP} 6.8 Hz) 2,53 (1H, dd, J_{HH} 10.0 Hz, J_{HP} 21,0 Hz) 3,84 (1H, ddd, J_{HH} = J_{HH} 2.5 Hz, J_{HH} 10,4 Hz) 5,56 (1H, m); ^{31}P n.m.r. 30,94; ^{13}C n.m.r. 13,8 (2 × Me, q, J_{CH} 124.6 Hz) 29,2 (CH, d, J_{CH} 134.9 Hz) 50,7 (CH, dd, J_{CH} = J_{CP} 130.4 Hz) 73,5 (CH, d, J_{CH} 144.0 Hz); MS, m/z 304 (M^+, 2,2%), 261 (15,4%), 243 (3,2%), 232 (100,0%), 204 (20,6%), 176 (23,2%), 91 (47,4%), 79 (24,1%).

(iii) From cyclohexylcarboxaldehyde. RS(SR) diethyl 1-(cyclohexen-1′-yl)-2-hydroxy-2-cyclohexylethylphosphonate (**1l**), purified and separated by chromatography (prep. t.l.c.; ether/hexane; 1:1); (43,0%) [70]) as an oil; ^{1}H n.m.r. ($CDCl_3$) 0,92 (2H, m) 1,01 (4H, m) 1,52 (4H, m) 1,97 (1H, m) 2,51 (1H, dd, J_{HH} 4.0 Hz, J_{HP} 25.2 Hz) 3,66 (1H, dd, J_{HH} 4.1 Hz, J_{HH} 6.4 Hz) 5,74 (1H, m); ^{31}P n.m.r. 30,09; ^{13}C n.m.r. 23,6 (CH_2, t, J_{CH} 127.4 Hz) 24,2-29,5 (4 × CH_2, m) 40,2 (CH, d, J_{CH} 125.5 Hz) 47,9 (CH, dd, J_{CH} = J_{CP} 129.7 Hz) 74,1 (CH, d, J_{CH} 142.0 Hz); MS, m/z 343 (M^+, 6,9%), 314 (11,8%), 231 (86,5%), 218 (93,5%), 162 (45,7%), 93 (79,0%), 79 (100%).

(iv) From phenylacetaldehyde. Two diastereoisomers of diethyl 1-(cyclohexen-1′-yl)-2-hydroxy-3-phenylpropylphosphonate (**1m**), purified and separated by chromatography (prep t.l.c.; diethyl ether/hexane; 1:1); (83,7% [95]) of which the RS(SR) isomer was an oil; ν_{max} ($CHCl_3$) 3571, 3413, 1672, 1608 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 2,42 (1H, dd, J_{HH} 4.0 Hz, J_{HP} 24.3 Hz) 2,84 (2H, d, J_{HH} 6.6 Hz) 4,34 (1H, ddt, J_{HH} = J_{HH} 6.3 Hz, J_{HP} 4.1 Hz) 5,81 (1H, m) 7,22 (5H, m); ^{31}P n.m.r. 29,21; ^{13}C n.m.r. 40,8 (CH_2, t, J_{CH} 127.2 Hz) 50,2 (CH, dd, J_{CH} = J_{CP} 127.6 Hz) 71,1 (CH, d, J_{CH} 144.3 Hz) 126,2 (CH, d, J_{CH} 159.0 Hz) 128,2 (2 × CH, d, J_{CH} 151.4 Hz) 129,3 (2 × CH, d, J_{CH} 156.3 Hz) 138,5 (C, s) and the RR (SS) stereoisomer colourless crystals, m.p. (from hexane) 90,7–90,9°C; ^{1}H n.m.r. ($CDCl_3$) 2,47 (1H, dd, J_{HH} 9.5 Hz, J_{HP} 21.1 Hz) 2,54 (1H, dd, J_{HH} 8.8 Hz, J_{HH} 14.4 Hz) 2,93 (1H, dd, J_{HH} 2.7 Hz, J_{HH} 13.9 Hz) 4,21 (1H, ddt, J_{HH} 2.8, J_{HH} 9.5 Hz, J_{HP} 2.8 Hz) 5,67 (1H, m) 7,22 (5H, m); ^{31}P n.m.r.

29,65; ^{13}C n.m.r. 40,8 (CH_2, t, J_{CH} 128.7 Hz) 50,1 (CH, dd, J_{CH} = J_{CP} 127.6 Hz) 70,9 (CH, d, J_{CH} 144.7 Hz) 125,9 (CH, d, J_{CH} 160.0 Hz) 128,0 (2 × CH, d, J_{CH} 153.8 Hz) 129,1 (2 × CH, d, J_{CH} 157.6 Hz) 138,4 (C, s); MS, m/z 352 (M^+, 2,5%), 261 (6,4%), 232 (100%), 197 (15,4%), 176 (15,0%), 91 (64,7%).

(v) From benzaldehyde. Two diastereoisomers of diethyl 1-(cyclohexen-1′-yl)-2-hydroxy-2-phenylethylphosphonate (**1n**), purified and separated by chromatography (prep t.l.c.; diethyl ether/hexane; 1:1); (84,7% [90]) of which the RS(SR) stereoisomer was an oil; ^{1}H n.m.r. ($CDCl_3$) 2,56 (1H, dd, J_{HH} 5.1 Hz, J_{HP} 23.2 Hz) 5,14 (1H, dd, J_{HH} = J_{HP} 5.3 Hz) 5,79 (1H, m) 7,22 (5H, m); ^{31}P n.m.r.; 27,78; ^{13}C n.m.r. 53,0 (CH, dd, J_{CH} = J_{CP} 127.0 Hz) 71,8 (CH, d, J_{CH} 147.2 Hz) 126,2 (2 × CH, d, J_{CH} 158.3 Hz) 127,0 (CH, d, J_{CH} 159.8 Hz) 127,5 (2 × CH, d, J_{CH} 159.5 Hz) 141,4 (C, s) and the RR(SS) stereoisomer colourless crystals, m.p. (from hexane) 92,4–92,7°C; ^{1}H n.m.r. ($CDCl_3$) 2,61 (1H, dd, J_{HH} 9.8 Hz, J_{HP} 19.6 Hz) 4,92 (1H, dd, J_{HH} = J_{HP} 9.7 Hz) 5,56 (1H, m) 7,20 (5H, m); ^{31}P n.m.r.; 29,46; ^{13}C n.m.r. 53,7 (CH, dd, J_{CH} = J_{CP} 127.4 Hz) 73,9 (CH, d, J_{CH} 148.0 Hz) 126,5 (2 × CH, d, J_{CH} 148.2 Hz) 127,1 (CH, d, J_{CH} 153.3 Hz) 127,4 (2 × CH, d, J_{CH} 153.6 Hz) 142,0 (C, s); MS, m/z 338 (M^+, 3,0%), 321 (29,9%), 308 (100,0%), 260 (28,3%), 232 (63,7%), 190 (83,9%), 169 (94,2%), 107 (94,1%), 93 (81,7%), 83 (96,6%).

(vi) From acrolein. Two diastereoisomers of diethyl 1-(cyclohexen-1′-yl)-2-hydroxybuten-3-ylmethylphosphonate (**1o**), purified and separated by chromatography (prep. t.l.c.; diethyl ether); (77,8% [90]), as oils; ^{1}H n.m.r. ($CDCl_3$) 2,43 (1H, dd, J_{HH} 5.0 Hz, J_{HP} 23.6 Hz) 4,53 (1H, m) 5,11 (1H, d, J_{HH} 8.9 Hz) 5,31 (1H, d, J_{HH} 16.9 Hz) 5,63 (1H, m) 5,75 (1H, ddd, J_{HHt} 16.8 Hz, J_{HHc} 10.6 Hz, J_{HH} 5.9 Hz); ^{31}P n.m.r. 28,06 ppm; ^{13}C n.m.r. 52,5 (CH, dd, J_{CH} = J_{CP} 128.1 Hz) 70,8 (CH, d, J_{CH} 152.2 Hz) 115,4 (CH_2, t, J_{CH} 158.2 Hz) 138,1 (CH, d, J_{CH} 155.1 Hz) and ^{1}H n.m.r. ($CDCl_3$) 2,41 (1H, dd, J_{HH} 9.6 Hz, J_{HP} 20.2 Hz) 4,40 (1H, m) 5,06 (1H, d, J_{HH} 8.9 Hz) 5,25 (1H, d, J_{HH} 17.1 Hz) 5,60 (1H, m) 5,75 (1H, ddd, J_{HHt} 16.8 Hz, J_{HHc} 10.6 Hz, J_{HH} 6,2 Hz); ^{31}P n.m.r. 29,30; ^{13}C n.m.r. 52,5 (CH, dd, J_{CH} = J_{CP} 128.4 Hz) 71,2 (CH, d, J_{CH} 146.5 Hz) 115,4 (CH_2, t, J_{CH} 158.2 Hz) 138,1 (CH, d, J_{CH} 155.3 Hz); MS, m/z 289 (M^+, 10,6%), 271 (47,9%), 232 (9,5%), 204 (9,0%), 176 (15,6%), 133 (100%), 91 (25,8%).

(C) Addition to diethyl 1-(cyclohexen-1′-yl)ethylphosphonate (**2c**).

(i) From benzaldehyde. Two diastereoisomers of diethyl 1-(cyclohexen-1′-yl)-1-methyl-2-hydroxy-2-phenylethylphosphonate (**1p**), purified and separated by chromatography (prep t.l.c.; diethyl ether/hexane; 1:1); (50,4% [70]) of which one was crystalline, m.p. (from hexane) 113,1–113,4°C; ^{1}H n.m.r. ($CDCl_3$) 1,06 (3H, d, J_{HP} 17.1 Hz) 5,28 (1H, d, J_{HH} 7.6 Hz) 5,64 (1H, m) 7,20 (5H, m); ^{31}P n.m.r. 29,51; ^{13}C n.m.r. 12,1 (Me, q, J_{CH} 129.5 Hz) 51,1 (C_1, d, J_{CP} 133.1 Hz) 74,8 (CH, d, J_{CH} 147.6 Hz) 126,4 (CH, d, J_{CH} 159.2 Hz) 126,8 (2 × CH, d, J_{CH} 158.9 Hz) 127,6 (2 × CH, d, J_{CH} 158.2 Hz) 140,1 (C, s) and the other an oil; ^{1}H n.m.r. ($CDCl_3$) 1,08 (3H, d, J_{HP} 16.3 Hz) 5,00 (1H, d, J_{HH} 5.4 Hz) 6,06 (1H, m) 7,24 (5H, m); ^{31}P n.m.r. 30,87; ^{13}C n.m.r. 13,9 (Me, q, J_{CH} 124.4 Hz) 49,5 (C_1, d, J_{CP} 132.7 Hz) 76,6 (CH, d, J_{CH} 146.9 Hz) 127,0 (2 × CH, d, J_{CH} 159.5 Hz) 127,5 (CH, d, J_{CH} 159.6 Hz) 128,4 (2 × CH, d, J_{CH} 158.6 Hz) 139,2 (C, s); MS, m/z 260 (M^+, 33,4%), 246 (69,7%), 232 (12,3%), 122 (31,2%), 105 (100,0%), 91 (40,6%).

(D) Addition to diethyl 1-(cyclohexen-1′-yl)-2-methylpropylphosphonate (**2d**).

Procedure A. The same procedure was followed as before.

(i) From propionaldehyde. Two diastereoisomers of diethyl 1-[2′-(1″-hydroxypropyl)cyclohexylidenyl]-2-methylpropylphosphonate (**3b**), purified and separated by chromatography (column; methylene dichloride); (69,1% [85]), as oils; ν_{max} ($CHCl_3$) 3601, 3403, 1587 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 0,94 (3H, t, J_{HH} 7.3 Hz) 1,13 (3H, d, J_{HH} 7.0 Hz) 1,15 (3H, d, J_{HH} 7.0 Hz) 1,30–2,00 (12H, m) 3,09 (1H, m); ^{31}P n.m.r. 22,11; ^{13}C n.m.r. 10,8 (2 × Me, q, J_{CH} 122.3 Hz) 20,6 (CH_2, t, J_{CH} 127.3 Hz) 20,9 (CH_2, t, J_{CH} 126.3 Hz) 22,6 (CH_2, t, J_{CH} 126.3 Hz) 27,8 (CH_2, t, J_{CH} 123.7 Hz) 28,5 (CH_2, t, J_{CH} 122.8 Hz) 29,3 (CH, d, J_{CH} 121.8) 46,3 (CH, d, J_{CH} 128.1 Hz) 71,1 (CH, d, J_{CH} 139.4 Hz) 129,2 (C_1, d, J_{CP} 164.9 Hz) 158,2 ($C_{1'}$, s) and ^{1}H n.m.r. ($CDCl_3$) 0,96 (3H, t, J_{HH} 7.3 Hz) 1,14 (3H, d, J_{HH} 7.0 Hz) 1,16 (3H, d, J_{HH} 7.0 Hz) 1,30–2,00 (12H, m) 3,17 (1H, m); ^{31}P n.m.r. 22,23; ^{13}C n.m.r. 10,5 (2 × Me, q, J_{CH} 127.3 Hz) 20,6 (CH_2, t, J_{CH} 127.3 Hz) 20,9 (CH_2, t, J_{CH} 126.3 Hz) 22,6 (CH_2, t, J_{CH} 126.3 Hz) 27,8 (CH_2, t, J_{CH} 123.7 Hz) 28,5 (CH_2, t, J_{CH} 122.8 Hz) 29,3 (CH, d, J_{CH} 121.8) 46,3 (CH, d, J_{CH} 128.1 Hz) 71,1 (CH, d, J_{CH} 139.4 Hz) 127,1 (C_1, d, J_{CP} 159.1 Hz) 157,4 ($C_{1'}$, s); MS, m/z 317 (M^+, 1,0%), 303 (6,7%), 274 (81,1%), 231 (46,7%), 203 (54,7%), 161 (27,0%), 133 (54,7%), 119 (50,2%), 93 (85,3%), 81 (84,1%), 41 (100,0%).

Procedure B

(**2d**) and butyllithium, in dry THF, were stirred at −78°C for 1 h whereupon propionaldehyde was added slowly. Stirring was continued for 6 h whilst the temperature was maintained at −78°C. After aqueous quenching, at the same temperature, and the usual work-up, the reaction mixture afforded an oil which, after chromatography (prep t.l.c.; diethyl ether/hexane; 1:1), yielded two diastereoisomers of diethyl 1-isopropyl-1-(cyclohexen-1′-yl)-2-hydroxybutylphosphonate (**1q**) (32,9% [60]), as oils; ^{1}H n.m.r. ($CDCl_3$) 1,02 (3H, d, J_{HH} 6.9 Hz) 1,11 (3H, t, J_{HH} 7.3 Hz) 1,19 (3H, d, J_{HH} 6.9 Hz) 1,55 (1H, m) 1,71 (1H, dq, J_{HH} 7.3 Hz, J_{HH} 6.8 Hz) 2,42 (1H, dq, J_{HH} 7.3 Hz, J_{HH} 6.7 Hz) 3,85 (1H, m) 5,79 (1H, m); ^{31}P n.m.r. 33,80 and ^{1}H n.m.r. ($CDCl_3$) 0,98 (3H, d, J_{HH} 6.9 Hz) 1,00 (3H, t, J_{HH} 7.3 Hz) 1,23 (3H, d, J_{HH} 6.9 Hz) 1,53 (1H, m) 1,76 (1H, dq, J_{HH} 6.8 Hz, J_{HH} 7.3 Hz) 2,28 (1H, dq, J_{HH} 6.7 Hz, J_{HH} 7.3 Hz) 3,87 (1H, m) 5,50 (1H, m); ^{31}P n.m.r. 34,53; ^{13}C n.m.r. 12,1 (Me, q, J_{CH} 125.7 Hz) 18,9 (2 × Me, q, J_{CH} 126.0 Hz) 19,7 (CH_2, t, J_{CH} 126.1 Hz) 31,4 (CH, d, J_{CH} 129.7 Hz) 53,2 (C_1, d, J_{CP} 130.1 Hz) 75,1 (CH, d, J_{CH} 145.9 Hz); MS, m/z 314 (M^+, 51,1%), 299 (13,9%), 274 (40,9%), 259 (56,3%), 232 (67,9%), 176 (80,1%), 161 (86,7%), 93 (91,8%), 55 (95,4%), 41 (100,0%).

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