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Palladium Catalysed Allylic Acetoxylation of Dialkyl Allyl Phosphonates.

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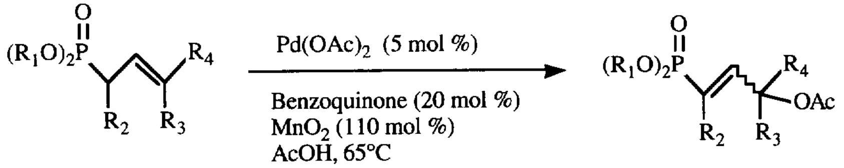
The catalytic acetoxylation of dialkyl allyl phosphonates with the $Pd(OAc)_2$/benzoquinone/MnO_2/HOAc system leads, regioselectively, to dialkyl 3-acetoxy 1-alkenyl phosphonates. On the basis of the regio- and stereoselectivity of the reaction, a mechanism is proposed which involves a (π-allyl) palladium complex as intermediate.

The palladium-catalysed oxidation of alkenes is an important reaction in organic synthesis, the Wacker process being the most famous example.[1] Among this class of reactions, the acetoxylation of olefins [2] constitutes a useful preparation of allylic acetates which have become important synthetic intermediates.[3]

Although the scope and limitations of these reactions have been extensively studied, the use of heteroatom-substituted olefins as substrates has received only limited attention : the acetoxylation of allylic sulfones is regio-and stereoselective and yields γ-acetoxy (*E*) α,β-unsaturated sulfones.[4] The same trends were reported by Tsuji [5] during his study on the palladium-catalysed acetoxylation of β,γ-unsaturated esters.

Having in mind the fact that allylic acetates possessing a phosphonyl group should constitute useful synthons, we decided to subject several β,γ-unsaturated phosphonates to allylic oxidation. We wish to disclose here our first results on the use of dialkyl allyl phosphonates as substrates in the palladium-catalysed acetoxylation using benzoquinone and manganese dioxide as reoxidants (Eq. 1).[6]



(Eq. 1)

The reaction occurs regioselectively with migration of the double bond to the α,β-position, thus affording exclusively dialkyl 3-acetoxy 1-alkenyl phosphonates as a mixture of *E* and *Z* isomers (Table).

Table: Acetoxylation of Allyl Phosphonates with the $Pd(OAc)_2$/benzoquinone/ MnO_2 system.

Entry	Compound	Reaction time (h) (a)	Conversion (%) (b)	Yield (%) (c)	*E/Z* (d)
1	R_1 = Me R_2 = R_3 = R_4 = H	4	100	75	85:15
2	R_1 = Et R_2 = R_3 = R_4 = H	6	100	70	90:10
3	R_1 = iPr R_2 = R_3 = R_4 = H	9	100	64	93:7
4	R_1 = nBu R_2 = R_3 = R_4 = H	10	100	58	90:10
5	R_1 = Me; R_2 = H R_3 = H; R_4 = Me	24	100	72	91:9
6	R_1 = Et; R_2 = H R_3 = H; R_4 = Me	30	100	65	100:0
7	R_1 = iPr; R_2 = H R_3 = H; R_4 = Me	32	100	70	100:0
8	R_1 = Et; R_2 = H R_3 = R_4 = Me	40	30 (e)	-	(f)
9	R_1 = Et; R_2 = H R_3 = H; R_4 = Ph	40	25 (e)	-	(f)
10	R_1 = Et; R_2 = Me R_3 = R_4 = H	28	100	70	65:35

(a) : Optimized. (b) : Determined by GLC analysis of aliquots. (c) : Of pure product. (d) : Determined by GLC and ^{31}P NMR of the crude products. (e) : The reactions stopped after 40 hours and conversion did not increase on further heating. (f) : Because of the presence of several minor by-products and mostly unreacted starting material, two successive chromatographic purifications were necessary to isolate pure products in very low yields (see experimental). They were obtained only as *E* isomers.

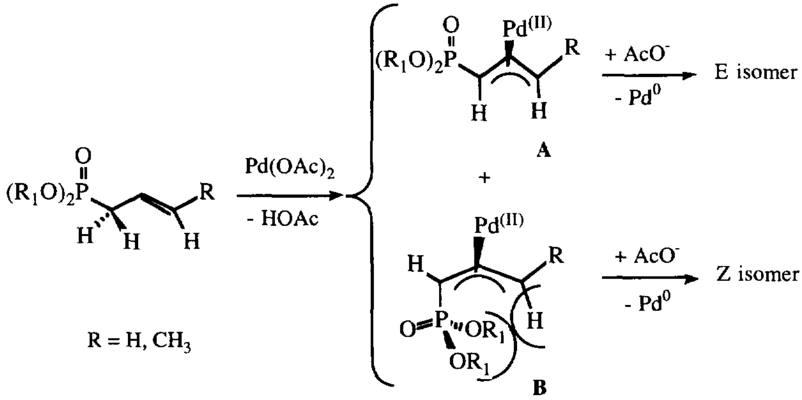
The reaction rate is influenced rather by the steric hindrance on the allyl moiety than by the size of substituents at phosphorus. Thus, the presence of two methyl groups (entry 8) or a phenyl group (entry 9) at the terminal position of the double bond strongly inhibits the reaction which stopped after ca. 25-30 % conversion (most of the starting material remained unchanged), whereas increasing bulk at phosphorus (from methyl to isopropyl, compare entries 1-4) has a weaker effect on the reaction time, and always leads to 100% conversion.

The *E*/*Z* ratios depend equally on both factors since increasing the size of the phosphorus groups from methyl to isopropyl or butyl (entries 1-4) or replacing a proton on the double bond by a methyl group (entry 1 vs. entry 5, 2 vs 6, 3 vs 7) results in high (or complete) *E* stereoselectivity.

In order to explain such stereoselectivities, it is crucial to understand the mechanism of the palladium catalysed allylic acetoxylation of olefins which, unfortunately, has not been definitively elucidated. This reaction is known to proceed *via* two possible mechanisms : (i) the 1,2 acetoxypalladation followed by β-elimination of palladium hydride and (ii) transformation of the alkene into a (π–allyl) palladium complex followed by nucleophilic attack of acetate. The acetoxypalladation process is favoured for terminal alkenes,[7] whereas competition between the two proposed mechanisms seems to occur in the case of internal acyclic and cyclic olefins.[2] Similar features were recently reported during the palladium-catalysed acrylation of olefins.[8] Furthermore, the quinone-based palladium catalysed acetoxylation of cyclohexene has been shown to proceed *via* a (π–allyl) palladium complex.[9]

The fact that our reactions occur with complete regioselectivity may indicate the existence of a (π-allyl) palladium complex as intermediate, as already postulated for the acetoxylation of β,γ unsaturayed esters.[5] This assumption is supported by the fact that such complexes are easily prepared [10] by reaction between a dialkyl allyl phosphonate and $PdCl_2$.

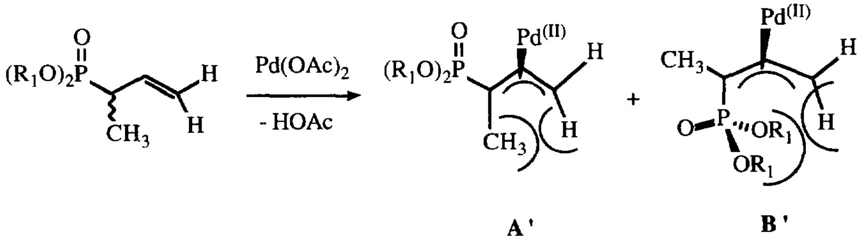
In our case, substitution of this (π-allyl) complex by acetate would be the crucial step in which the regioselectivity is determined, probably owing to the electronic distribution in this complex as well as the tendency of the double bond to be conjugated with the phosphonyl group. The reactivity of such complexes with different nucleophiles has been documented,[10] and exhibits the same features, i.e. exclusive formation of the conjugated phosphonate. The stereoselectivity can easily be explained with this model. Thus, the formation of *E* and *Z* isomers may occur *via* complexes **A** (syn, syn) and **B** (anti, syn), respectively, as depicted in Scheme I.



Scheme I

Although **A** and **B** may be in equilibrium via a π-σ-π isomerisation,[11] **B** is thermodynamically less favoured than **A** because of the steric repulsion between the phosphorus substituents and those at the terminus of the allyl moiety. This repulsion obviously increases with the steric bulk of these groups, and hence accounts for the concomitant increasing *E*/*Z* ratio.[12]

On the other hand, the presence of a methyl group α to phosphorus (entry 10) corroborates this hypothesis since the energetic difference between **A'** and **B'** (Scheme II) is reduced because of the less discriminative repulsion between the methyl and the phosphonyl groups. The higher steric bulk of this methyl (compared to a proton) leads to a higher proportion of Z isomer .



Scheme II

In summary, the reactions reported here complement the data previously described on the palladium-catalysed acetoxylation of functionalized olefins. Although we have no evidence for the existence of a (π-allyl) palladium complex as intermediate in our reactions, the exclusive formation of 3-acetoxy 1-alkenyl phosphonates may be a valuable argument for this mechanism. However, this question requires further studies on isolated complexes.

Nevertheless, these results constitute a short synthesis of 3-acetoxy 1-alkenyl phosphonates which, due to their different functionalities, should become useful synthons. Although another approach to these compounds relies on the base-promoted ring opening of dialkyl 2,3-epoxy phosphonates,[13] our method appears to be more general. The use of these new compounds may be exemplified through Wadsworth Emmons reactions as well as the palladium-catalysed nucleophilic substitution.[14]

Furthermore, the presence of chiral groups at phosphorus on the starting allyl phosphonate may lead to an useful enantioselective version of this reaction, since the use of chiral ligands for palladium in acetoxylation has, until now, met with little success.[15]

Work along these lines is in progress and further synthetic applications of 3-acetoxy 1-alkenyl phosphonates will be reported in due course.

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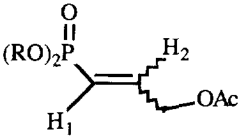
EXPERIMENTAL SECTION

Commercially available reagents and solvents were used without further purification. MnO_2 was used without prior activation. Flash chromatography was carried out using Merck Kiesegel 60H silica. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, on a Bruker AC 200 spectrometer at 200.00 MHz and 50.36 MHz, respectively (the usual abbreviations are used : s = singulet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sx = sextuplet, o = octuplet, m=multiplet). The positive chemical shift values (ppm) are downfield from tetramethylsilane as internal standard. ^{31}P NMR spectra were recorded in $CDCl_3$, on a Bruker AC 100 spectrometer at 40.54 MHz, with 85% H_3PO_4 as external standard. Infrared spectra were recorded on a 16 PC (IRFT) Perkin Elmer spectrometer as thin films. Elemental analyses were performed by the Service de Microanalyse de la Faculté de St Jérôme. The starting dialkyl allyl phosphonates were prepared *via* a Michaelis Arbuzov reaction between the corresponding trialkyl phosphites and allylic bromides,[16] except diethyl 1-methyl 2-propenyl phosphonate which was obtained by alkylation of diethyl allyl phosphonate, see ref. 17 for a similar reaction. E and Z structures were attributed by examination of $^3J_{H1H2}$ and $^3J_{PH2}$ for the isolated isomers and by comparison with reported data.[18]



General procedure for the acetoxylation of allyl phosphonates:

A mixture of palladium acetate (63 mg; 0.28 mmol; 0.05 eq.), benzoquinone (121 mg; 1.12 mmol; 0.2 eq.), and MnO_2 (540 mg; 6.2 mmol; 1.1 eq.) in acetic acid (2 ml) was stirred at 65°C for 10 minutes. Diethyl allyl phosphonate (1.0 g; 5.6 mmol; 1 eq.) dissolved in acetic acid (2 ml) was added, and heating was continued. After the end of the reaction (see Table), the mixture was cooled to room temperature, diluted with EtOAc and filtered over a pad of Celite which was rinsed with EtOAc. The residue obtained after removal of solvents was purified by flash chromatography on silicagel with ethyl acetate.[19] When possible, *E* and *Z* isomers were further separated by chromatography on silica with ethyl acetate. Analytical samples were obtained by Kugelrohr distillation (0.05 Torr, 130-160°C air bath temperature).

Dimethyl (3-acetoxy 1-propenyl) phosphonate (entry 1). Colourless oil (found : C, 40.2; H, 6.5; O, 38.1; P, 14.7. $C_7H_{13}O_5P$ requires C, 40.4; H, 6.3; O, 38.5; P, 14.9). **IR** (cm^{-1}) : 1740, 1640, 1230, 1020.

***E* isomer** : ^1H NMR: 2.11 (s, $CH_3C{=}O$); 3.72 (d, CH_3O, $^3J_{PH}$=11.2 Hz); 4.72 (dt, CH_2, $^4J_{PH}$=3.9Hz, $^3J_{HH}$=3.9 Hz, $^4J_{HH}$=2.0 Hz); 5.86 (ddt, H_1, $^2J_{PH}$=19.3 Hz, $^3J_{HH}$=17.2 Hz, $^4J_{HH}$=2.0 Hz); 6.78 (ddt, H_2, $^3J_{PH}$=21.3 Hz, $^3J_{HH}$=17.2 Hz, $^3J_{HH}$=4.0 Hz); ^{31}P NMR: 19.1; ^{13}C NMR: 20.6 (s, $\underline{C}H_3C{=}O$); 52.4 (d, CH_3O, $^2J_{PC}$=5.9 Hz); 63.2 (d, CH_2O, $^3J_{PC}$=23.4 Hz);117.0 (d, $P\underline{C}H{=}C$, $^1J_{PC}$=190 Hz); 146.4 (d, $PCH{=}\underline{C}$, $^2J_{PC}$=7.1Hz); 170.0 (s, C=O).

***Z* isomer** : ^{31}P NMR: 16.9.

Diethyl (3-acetoxy 1-propenyl) phosphonate (entry 2). Colourless oil (found : C, 45.9; H, 7.4; O, 34.0; P, 13.2. $C_9H_{17}O_5P$ requires C, 45.8; H, 7.2; O, 33.9; P, 13.1). **IR** (cm^{-1}) : 1750; 1640; 1240; 1050.

***E* isomer** : ^{1}H NMR: 1.26 (t, $C\underline{H}_3CH_2$, $^3J_{HH}$=7.0 Hz); 2.05 (s, $CH_3C{=}O$); 4.02 (qt, CH_2OP, $^3J_{PH}$=7.0 Hz, $^3J_{HH}$=7.0 Hz); 4.65 (m, $CH_2OC{=}O$); 5.74 (ddt, H_1, $^2J_{PH}$=19.2 Hz, $^3J_{HH}$=17.3 Hz, $^4J_{HH}$=2.0 Hz); 6.68 (ddt, H_2, $^3J_{PH}$=22.4 Hz, $^3J_{HH}$=17.3 Hz, $^3J_{HH}$=4.1 Hz); ^{31}P NMR: 16.3; ^{13}C NMR: 16.2 (d, $\underline{C}H_3CH_2$, $^3J_{PC}$=6.4 Hz); 20.6 (s, $\underline{C}H_3C{=}O$); 61.9 (d, $\underline{C}H_2OC{=}0$, $^3J_{PC}$=5.4 Hz); 63.3 (d, CH_2OP, $^2J_{PC}$=23.5 Hz); 117.9 (d, $P\underline{C}H{=}C$, $^1J_{PC}$=189.6 Hz); 145.5 (d, $PCH{=}\underline{C}$, $^2J_{PC}$=6.4 Hz); 170.0 (s, C=O).

***Z* isomer** : ^{1}H NMR: 1.27 (t, $C\underline{H}_3CH_2$, $^3J_{HH}$=7.0 Hz); 2.03 (s, $CH_3C{=}O$); 4.03 (qt, CH_2OP, $^3J_{PH}$=7.0 Hz, $^3J_{HH}$=7.0 Hz); 5.10 (m, $CH_2OC{=}O$); 5.70 (ddt, H_1, $^2J_{PH}$=17.0 Hz, $^3J_{HH}$=13.5 Hz, $^4J_{HH}$=1.9 Hz); 6.49 (ddt, H_2, $^3J_{PH}$=51.0 Hz, $^3J_{HH}$=13.5 Hz, $^3J_{HH}$=5.9 Hz); ^{31}P NMR: 14.0; ^{13}C NMR: 16.2 (d, $\underline{C}H_3CH_2$, $^3J_{PC}$=6.2 Hz); 20.7 (s, $\underline{C}H_3C{=}O$); 61.7 (d, $\underline{C}H_2OC{=}O$, $^3J_{PC}$=5.4 Hz); 62.0 (d, CH_2OP, $^2J_{PC}$=7.8 Hz); 119.0 (d, $P\underline{C}H{=}C$, $^1J_{PC}$=182.0 Hz); 146.8 (d, $PCH{=}\underline{C}$, $^2J_{PC}$=2.6 Hz); 170.5 (s, C=O).

Diisopropyl (3-acetoxy 1-propenyl) phosphonate (entry 3). Colourless oil (found : C, 50.0; H, 7.9; O, 30.2; P, 11.4. $C_{11}H_{21}O_5P$ requires C, 50.0; H, 8.0; O, 30.3; P, 11.7). **IR** (cm^{-1}) : 1740, 1630, 1240, 1020.

***E* isomer** : ^{1}H NMR: 1.31 (d, $C\underline{H}_3CHO$, $^3J_{HH}$=6.3 Hz); 1.34 (d, $C\underline{H}_3CHO$, $^3J_{HH}$=6.3 Hz); 2.11 (s, $CH_3C{=}O$); 4.70 (m, CHOP); 4.70 (m, $CH_2OC{=}O$); 5.90 (ddt, H_1, $^2J_{PH}$=18.7 Hz, $^3J_{HH}$=17.3 Hz, $^4J_{HH}$=2.1 Hz); 6.73 (ddt, H_2, $^3J_{PH}$=22.3 Hz, $^3J_{HH}$=17.3 Hz, $^3J_{HH}$=4.2 Hz); ^{31}P NMR: 14.2; ^{13}C NMR: 20.7 (s, $\underline{C}H_3C{=}O$); 24.1 (d, $\underline{C}H_3CH$, $^3J_{PC}$=4.9 Hz); 63.5 (d, $\underline{C}H_2OC{=}O$, $^3J_{PC}$=11.8 Hz); 70.7 (d, CHOP, $^2J_{PC}$=5.6 Hz); 119.8 (d, $P\underline{C}H{=}C$, $^1J_{PC}$=188.6 Hz); 144.4 (d, $PCH{=}\underline{C}$, $^2J_{PC}$=6.0 Hz); 170.3 (s, C=O).

***Z* isomer** :^{31}P NMR: 12.0.

Dibutyl (3-acetoxy 1-propenyl) phosphonate (entry 4). Colourless oil (found : C, 53.2; H, 8.6; O, 27.6; P, 10.4. $C_{13}H_{25}O_5P$ requires C, 53.4; H, 8.6; O, 27.4; P, 10.6). **IR** (cm^{-1}) : 1740; 1640; 1230; 1010.

***E* isomer** : ^{1}H NMR: 0.95 (t, $C\underline{H}_3CH_2$, $^3J_{HH}$=7.0 Hz); 1.45 (sx, $CH_3C\underline{H}_2$, $^3J_{HH}$=7.0 Hz); 1.65 (qt, $C\underline{H}_2CH_2O$, $^3J_{HH}$=7.0); 2.15 (s, $CH_3C{=}O$); 4.05 (q, $C\underline{H}_2OP$, $^3J_{PH}$=6.9 Hz, $^3J_{HH}$=6.9 Hz); 4.75 (ddd, $CH_2OC{=}O$, $^3J_{HH}$=4.1 Hz, $^4J_{PH}$=3.5 Hz, $^4J_{HH}$=2.0 Hz); 5.90 (ddt, H_1, $^2J_{PH}$=19.2 Hz, $^3J_{HH}$=17.3 Hz, $^4J_{HH}$=2.0); 6.80 (ddt, H_2, $^3J_{PH}$=22.4 Hz, $^3J_{HH}$=17.3 Hz, $^3J_{HH}$=4.1 Hz); ^{31}P NMR: 16.5; ^{13}C NMR: 13.3 (s, $\underline{C}H_3CH_2$); 20.4 (s, $\underline{C}H_3C{=}O$); 32.0 (s, $CH_3\underline{C}H_2$) ;32.3 (s, $\underline{C}H_2CH_2O$); 63.2 (d, CH_2OP, $^2J_{PC}$=23.8 Hz); 65.4 (d, $CH_2OC{=}O$, $^3J_{PC}$=6.0 Hz); 117.8 (d, $P\underline{C}H{=}C$, $^1J_{PC}$=188.2 Hz) ;145.2 (d, $PCH{=}\underline{C}$, $^2J_{PC}$=6.1 Hz); 169.8 (s, C=O).

***Z* isomer** : ^{31}P NMR: 14.3.

Dimethyl (3-acetoxy 1-butenyl) phosphonate (entry 5). Colourless oil (found : C, 43.0; H, 6.8; O, 36.3; P, 14.0. $C_8H_{15}O_5P$ requires C, 43.2; H, 6.8; O, 36.0; P, 14.0). **IR** (cm^{-1}) : 1740; 1640; 1240; 1050.

***E* isomer** : ^{1}H NMR: 1.31 (d, $C\underline{H}_3CH_2$, $^3J_{HH}$=6.7 Hz); 2.04 (s, $CH_3C{=}O$); 3.68 (d, CH_3O, $^3J_{PH}$=11.2 Hz); 5.41 (dt, CHO, $^4J_{PH}$=3.9 Hz, $^3J_{HH}$=3.9 Hz, $^4J_{HH}$=2.0 Hz); 5.74 (ddd, H_1, $^2J_{PH}$=19.3 Hz, $^3J_{HH}$=17.2

Hz, $^4J_{HH}$=2.0 Hz); 6.68 (ddd, H_2, $^3J_{PH}$=21.3 Hz, $^3J_{HH}$=17.2 Hz, $^3J_{HH}$=4.0 Hz); ^{31}P NMR: 19.8; ^{13}C NMR: 16.3 (d, CH_3CH, $^4J_{PC}$=6.2 Hz); 20.1 (s, CH_3C=O); 52.1 (d, CH_3O, $^2J_{PC}$=6.0 Hz); 69.2 (d, CHO, $^3J_{PC}$=22.0 Hz); 114.7 (d, PCH=C, $^1J_{PC}$=188 Hz); 146.4 (d, PCH=C, $^2J_{PC}$=5.9 Hz); 170.0 (s, C=O).
***Z* isomer** : ^{1}H NMR: 1.30 (d, CH_3CH, $^3J_{HH}$=6.7 Hz); 2.04 (s, CH_3C=O); 3.70 (d, CH_3O, $^3J_{PH}$=11.0 Hz); 5.62 (m, CHO); 5.75 (ddd, H_1, $^2J_{PH}$=17.0 Hz, $^3J_{HH}$=13.4 Hz, $^4J_{HH}$=1.9 Hz); 6.40 (ddd, H_2, $^3J_{PH}$=53.1 Hz, $^3J_{HH}$=13.4 Hz, $^3J_{HH}$=8.3 Hz); ^{31}P NMR: 17.5.

(*E*)- Diethyl (3-acetoxy 1-butenyl) phosphonate (entry 6). Colourless oil (found : C, 47.7; H, 7.7; O, 31.8; P, 12.4. $C_{10}H_{19}O_5P$ requires C, 48.0; H, 7.6; O, 32.0; P, 12.4). **IR** (cm^{-1}) : 1740, 1630, 1240, 1020. ^{1}H NMR: 1.34 (t, CH_3CH_2, $^3J_{HH}$=7.0 Hz); 1.36 (d, CH_3CH, $^3J_{HH}$=6.9 Hz); 2.10 (s, CH_3C=O); 4.10 (qt, CH_2OP, $^3J_{PH}$=7.1 Hz, $^3J_{HH}$=7.1 Hz); 5.45 (m, CHOC=O); 5.85 (ddd, H_1, $^2J_{PH}$=19.0 Hz, $^3J_{HH}$=17.3 Hz, $^4J_{HH}$=1.7 Hz); 6.49 (ddd, H_2, $^3J_{PH}$=21.7 Hz, $^3J_{HH}$=17.3 Hz, $^3J_{HH}$=4.4 Hz); ^{31}P NMR: 16.9; ^{13}C NMR: 16.3 (d, CH_3CH, $^4J_{PC}$=6.2 Hz); 19.4 (s, CH_3CH_2); 20.1 (s, CH_3C=O); 61.9 (d, CH_2O, $^2J_{PC}$=6.0 Hz); 69.6 (d, CHO, $^3J_{PC}$=22.0 Hz); 116.7 (d, PCH=C, $^1J_{PC}$=188 Hz); 150.6 (d, PCH=C, $^2J_{PC}$=5.7 Hz); 170.0 (s, C=O).

(*E*)-Diisopropyl (3-acetoxy 1-butenyl) phosphonate (entry 7). Colourless oil (found : C, 51.6; H, 8.4; O, 29.0; P, 11.0. $C_{12}H_{23}O_5P$ requires C, 51.8; H, 8.3; O, 28.8; P, 11.2). **IR** (cm^{-1}) : 1740; 1640; 1230; 1010. ^{1}H NMR: 1.19 (d, CH_3CHO, $^3J_{HH}$=6.5 Hz); 1.21 (d, CH_3CHO, $^3J_{HH}$=6.5 Hz); 2.0 (s, CH_3C=O); 4.56 (o, CHOP, $^3J_{PH}$=6.3 Hz, $^3J_{HH}$=6.3 Hz); 5.35 (m, CHOC=O); 5.74 (ddd, H_1, $^2J_{PH}$=18.8 Hz, $^3J_{HH}$=17.2 Hz, $^4J_{HH}$=1.6 Hz); 6.58 (ddd, H_2, $^3J_{PH}$=21.8 Hz, $^3J_{HH}$=17.2 Hz, $^3J_{HH}$=4.5 Hz); ^{31}P NMR: 14.6; ^{13}C NMR: 19.3 (d, CH_3CHOC=O, $^3J_{PC}$=2.5 Hz); 20.9 (s, CH_3C=O); 23.9 (d, CH_3CH, $^3J_{PC}$=4.9 Hz); 69.6 (d, CHOC=O, $^3J_{PC}$=22.7 Hz); 70.5 (d, CHOP, $^2J_{PC}$=6.5 Hz); 118.3 (d, PCH=C, $^1J_{PC}$=189.7 Hz); 149.5 (d, PCH=C, $^2J_{PC}$=5.9 Hz); 169.8 (s, C=O).

(*E*)-Diethyl (3-acetoxy 3-methyl 1-butenyl) phosphonate (entry 8). Obtained in 3% yield as a colourless oil. (found : C, 50.0; H, 7.9; O, 30.1; P, 11.8. $C_{11}H_{21}O_5P$ requires C, 50.0; H, 8.0; O, 30.3; P, 11.7). **IR** (cm^{-1}) : 1745; 1635; 1230; 1015. ^{1}H NMR: 1.38 (t, CH_3CH_2O, $^3J_{HH}$=6.9 Hz); 1.65 (s, CH_3); 1.92 (s, CH_3C=O); 4.14 (qt, CH_2OP, $^3J_{PH}$=7.2 Hz, $^3J_{HH}$=7.2 Hz); 5.66 (dd, H_1, $^2J_{PH}$=17.8 Hz, $^3J_{HH}$=17.0 Hz); 7.16 (dd, H_2, $^3J_{PH}$=21.7 Hz, $^3J_{HH}$=17.0 Hz); ^{31}P NMR: 16.5.

(*E*)-Diethyl (3-acetoxy 3-phenyl 1-propenyl) phosphonate (entry 9). Obtained in 2% yield as a slightly yellow oil. (found : C, 57.6; H, 6.7; O, 25.4; P, 10.0. $C_{15}H_{21}O_5P$ requires C, 57.7; H, 6.7; O, 25.6; P, 9.9). **IR** (cm^{-1}) : 1730; 1640; 1220; 1010. ^{1}H NMR: 1.28 and 1.30 (t, CH_3CH_2O non equivalents, $^3J_{HH}$=7.0 Hz); 2.12 (s, CH_3C=O); 4.06 (m, CH_2OP); 5.88 (ddd, H_1, $^2J_{PH}$=19.0 Hz, $^3J_{HH}$=17.1 Hz, $^4J_{HH}$=1.8 Hz); 6.33(ddd, CHO, $^3J_{HH}$=4.7 Hz, $^4J_{PH}$=3.2 Hz, $^4J_{HH}$=1.8 Hz); 6.80 (ddd, H_2, $^3J_{PH}$=21.7 Hz, $^3J_{HH}$=17.1 Hz, $^3J_{HH}$=4.4 Hz); ^{31}P NMR: 18.9.

Diethyl (3-acetoxy 1-methyl 1-propenyl) phosphonate (entry 10). Slightly yellow oil (found : C, 47.9; H, 7.6; O, 31.8; P, 12.3. $C_{10}H_{19}O_5P$ requires C, 48.0; H, 7.6; O, 32.0; P, 12.4).
IR (cm^{-1}) : 1730, 1620, 1240, 1030.

***E* isomer** : ^{1}H NMR: 1.26 (t, $C\underline{H}_3CH_2$, $^3J_{HH}$=7.0 Hz); 1.79 (dd, CH_3C=, $^3J_{PH}$=14.8 Hz, $^4J_{HH}$=1.6); 2.0 (s, CH_3C=O); 4.03 (qt, CH_2OP, $^3J_{PH}$=7.0 Hz, $^3J_{HH}$=7.0 Hz); 4.65 (ddq,CH_2OC=O, $^4J_{PH}$=4.8 Hz, $^3J_{HH}$=4.8 Hz, $^5J_{HH}$=1.0 Hz); 6.45 (dtq, H_2, $^3J_{PH}$=23.4 Hz, $^3J_{HH}$=4.9 Hz, $^3J_{HH}$=1.6 Hz); ^{31}P NMR: 18.6.
***Z* isomer** : ^{1}H NMR: 1.30 (t, $C\underline{H}_3CH_2$, $^3J_{HH}$=7.0 Hz); 1.90 (dd, CH_3C=, $^3J_{PH}$=12.9 Hz, $^4J_{HH}$=1.5 Hz); 2.05 (s, CH_3C=O); 4.08 (qt, CH_2OP, $^3J_{PH}$=7.0 Hz, $^3J_{HH}$=7.0 Hz); 5.03 (m,CH_2OC=O); 6.15 (dtq, H_2, $^3J_{PH}$=48.7 Hz, $^3J_{HH}$=6.3 Hz, $^3J_{HH}$=1.7 Hz); ^{31}P NMR: 16.3.

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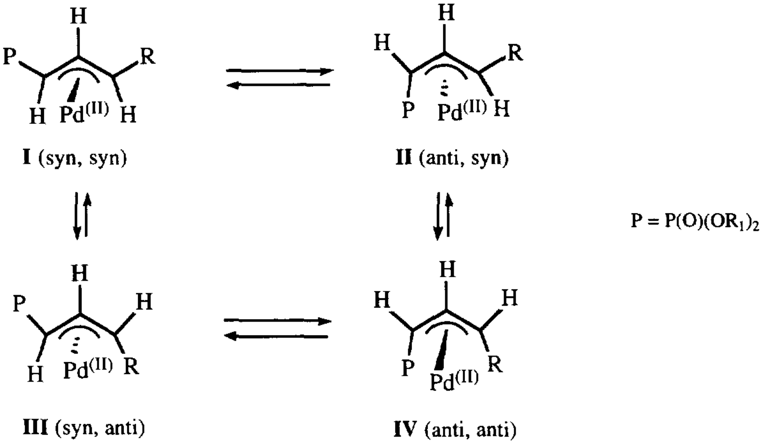
11. Only the relative position of the phosphonate group determines the stereoselectivity of the reaction, as shown in the following scheme.



Syn (π-allyl) palladium complexes **I** and **III** give rise to the E isomer, while Z isomer results from anti complexes **II** and **IV**.
Thus, syn/anti isomerisation can also occur on the γ position, but this phenomenon does not influence the *E*/*Z* ratios.

12. In a control experiment, pure *(E)* and *(Z)* diethyl 3-acetoxy 1-propenyl phosphonates were separately subjected to the acetoxylation conditions (see experimental, 65°C, overnight). No isomerisation occured in both cases, indicating that there is no thermodynamic equilibrium between the two isomeric acetates under the reactions conditions. Therefore, the stereochemical outcome of the reaction cannot be modified by such a process.

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19. The usual aqueous work up [2e] led to the formation of variable amounts of saponified phosphonates. Thus, aqueous work up of the crude acetoxylation mixture of diethyl allyl phosphonate gave 10-15% of diethyl 3-hydroxy 1-propenyl phosphonate whose spectral data were in accordance with those reported previously.[13]

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