Pergamon

Tetrahedron 56 (2000) 2693–2697

TETRAHEDRON

Palladium-Catalyzed Acetoxylation of Cyclic Allyl Phosphonates in the Presence of Isopentyl Nitrite and Using Molecular Oxygen as Final Oxidant

Mireille Attolini, Gilbert Peiffer and Michel Maffei*

Laboratoire des Organo-Phosphorés (E.S.A. 6009 du C.N.R.S.), B.P. 552, Faculté de Saint Jérôme, Avenue Escadrille Normandie Niémen, 13397 Marseille Cedex 20, France

Received 2 November 1999; accepted 24 February 2000

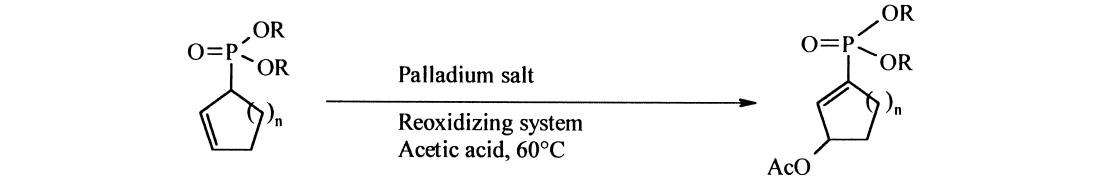
Abstract—The palladium-catalyzed acetoxylation of cyclic dialkyl allyl phosphonates is effected using palladium chloride as catalyst, in the presence of isopentyl nitrite in acetic acid under an oxygen atmosphere. The proposed mechanism for the reaction involves a palladium nitro–nitroso redox couple.

Introduction

The catalytic acetoxylation of alkenes is a useful and straightforward method for the preparation of allyl acetates,[1] which have become important synthetic intermediates.[2] We have recently described the Pd-catalyzed acetoxylation of dialkyl allyl phosphonates with benzoquinone and manganese dioxide as reoxidants,[3] which allows an easy, one step synthesis of dialkyl 3-acetoxy-1-alkenyl phosphonates. We further illustrated the synthetic utility of these products through the preparation of precursors of biologically active phosphono amino acids.[4] Dialkyl 3-acetoxy-1-alkenyl phosphonates can also be used to prepare the corresponding allyl alcohols which have, in turn, been used as starting materials for the synthesis of antiviral nucleosides[5] and optically active cyclopropyl ketones.[6]

We became interested in extending the scope of the acetoxylation reaction to cyclic allyl phosphonates **1–3** (Scheme 1) since the corresponding products, in light of the references cited above, would lead to useful synthetic intermediates.

When **1a** was subjected to the standard acetoxylation conditions (i.e. 5% $Pd(OAc)_2$, 20% benzoquinone, 110% MnO_2, acetic acid, 65°C), only ca. 30% of starting material was consumed after 65 h, and the expected acetate **4a** was formed with 48% selectivity, beside several by-products, as evidenced by ^{31}P NMR analysis of the crude product. The same reaction performed at 90°C led to a complete



n = 2	n = 1	n = 3
1a R = Et	**2a** R = Et	**3a** R = Et
1b R = Me		**3c** R = i-Pr
1c R = i-Pr		

n = 2	n = 1	n = 3
4a R = Et	**5a** R = Et	**6a** R = Et
4b R = Me		**6c** R = i-Pr
4c R = i-Pr		

Scheme 1.

Keywords: palladium-catalyzed acetoxylation; cyclic dialkyl allyl phosphonates; isopentyl nitrite; 3-acetoxy-1-alkenyl phosphonates.
* Corresponding author. Fax: +33-4-91-28-80-30; e-mail: michel.maffei@lop.u-3mrs.fr

0040–4020/00/$ - see front matter
PII: S0040-4020(00)00172-1

Table 1. Palladium-catalyzed acetoxylation of cyclic allyl phosphonates **1–3** in the presence of 5% $Pd(OAc)_2$, 20% benzoquinone, and 110% MnO_2, in acetic acid

Compound	Reaction time (h)	Temperature (°C)	Conversion (%)	Selectivity (%)[a]
1a	65	65	30	48
1a	20	90	100	34
2a	70	65	38	84
3a	40	65	20	40

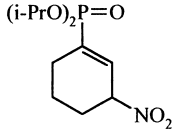
[a] For the acetoxylation product, measured by ^{31}P NMR of the crude.

conversion after 20 h, but the selectivity was lower (34%). Similar results were obtained with cyclopentenyl and cycloheptenyl phosphonates **2a** and **3a**, respectively (Table 1).

The use of benzoquinone alone (without MnO_2) did not improve the conversion and/or selectivity.

We thought that these low yields might result from an inefficient reoxidation of palladium. In order to check this assumption, we employed the conditions described by Tsuji (i.e. 10 mol% $PdCl_2$, 150 mol% isopentyl nitrite, acetic acid, oxygen atmosphere) for the acetoxylation of β,γ-unsatured esters,[7] in which isopentyl nitrite acts as the reoxidizing reagent. In this case, we were pleased to note that allyl phosphonates **1–3** were totally converted (Table 2), and the expected acetates **4–6** were obtained with moderate to good yields. It should be noted that the reactions started after a lag period of ca. 1.5 h. The use of palladium acetate instead of $PdCl_2$ gave less satisfactory results since the reaction was incomplete in all cases.

Although cyclopentenyl phosphonate **2a** affords the expected acetate **5a** as a single product, the acetoxylation of the six- (**1a**, **1b** and **1c**) and seven- (**3a** and **3c**) membered ring analogues still leads to side products (in lower amounts however), from which the acetoxyphosphonates are easily separated. In one case (Table 2, entry 3), the by product could be isolated in a pure state. Careful examination of its NMR data as well as its mass spectrum ($[M^+]=291$) and its infrared spectrum ($\nu=1540$ and 1395 cm^{-1}) led us to assign its structure as the 3-nitro derivative **7**.



7

In the case of the cycloheptenyl phosphonates, the low yields are attributed to the additional formation of (cyclohepten-1-yl) phosphonates, resulting from an isomerization[8] of the starting material.[†] These were found to be totally unreactive towards acetoxylation.

In order to assess the influence of both nitrite and oxygen on the reaction outcome, we carried out the experiments described below.

First, it appears that the presence of oxygen during the reaction is essential: thus, the acetoxylation of dimethyl cyclohexen-2-yl phosphonate **1b** is complete after 14 h under the conditions listed above (i.e. 10 mol% $PdCl_2$, 150 mol% isopentyl nitrite, acetic acid, oxygen atmosphere, 65°C), whereas the same reaction run in air needs 25 h to go to completion. Interestingly, in this last case, the lag period was increased to 3 h.

On the other hand, the influence of the amount of isopentyl nitrite on the reaction has been evaluated, again with **1b** as substrate (Table 3).

These experiments clearly show that only a small amount of nitrite is sufficient to drive the reaction to completion without altering appreciably the yields and reaction times. Thus, the use of only 20 mol% of isopentyl nitrite with respect to the substrate is sufficient to drive the reaction to completion.

These results led us to the conclusion that isopentyl nitrite may produce a palladium species easily oxidised by oxygen, resulting in an efficient recycling of Pd(0).

Table 2. Palladium-catalyzed acetoxylation of cyclic allyl phosphonates **1–3** in the presence of 10 mol% $PdCl_2$ and 150 mol% isopentyl nitrite in acetic acid under oxygen, 65°C

Entry	Substrate	Selectivity (%)[a]	Reaction time (h)	Yield (%)[b]
1	**1a**	82	14	70
2	**1b**	75	21	69
3	**1c**	70	19	65
4	**2a**	100	20	75
5	**3a**	48	17	43
6	**3c**	42	24	34

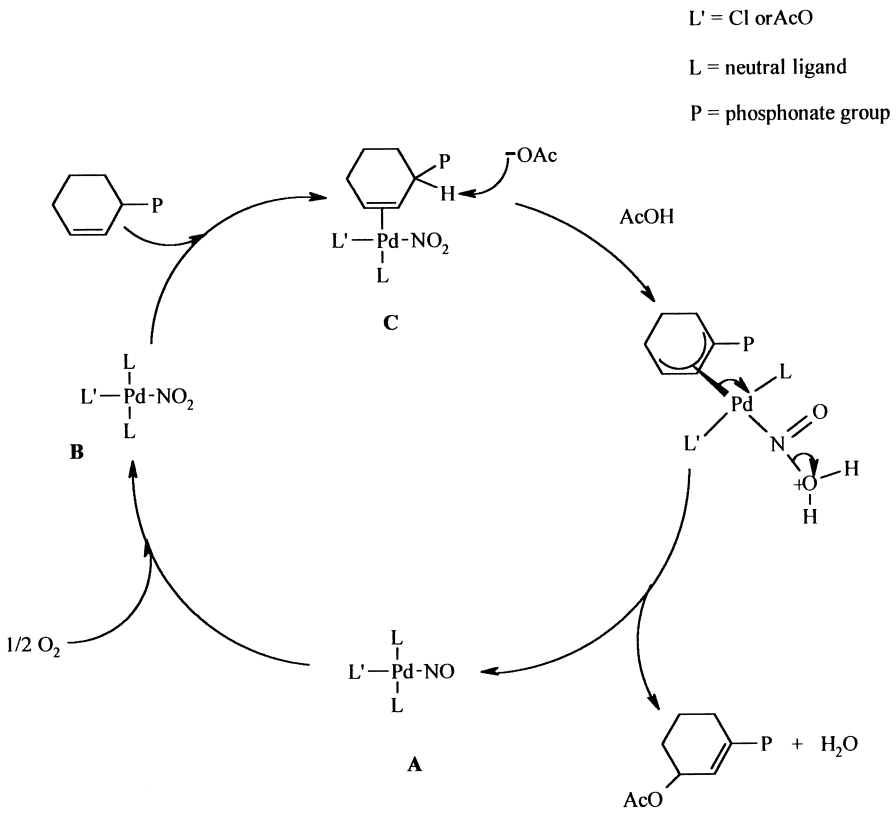
[a] For the acetoxylation product, measured by ^{31}P NMR of the crude.
[b] Of pure product.

Table 3. Influence of the amount of isopentyl nitrite on the Pd-catalyzed acetoxylation of **1b** (conditions: 10 mol% $PdCl_2$ in acetic acid under oxygen, 65°C, reaction time: 20 h)

Isopentyl nitrite (mol%)	Conversion (%)	Selectivity (%)[a]	Yield (%)[b]
500	100	70	60
150	100	75	69
50	100	80	74
20	100	80	72
0	0	–	–

[a] For the acetoxylation product, measured by ^{31}P NMR of the crude.
[b] Of pure product.

[†] This assumption was deduced from the examination of ^1H and ^{31}P NMR spectra of the crude product, which display several signals in agreement with an α,β-unsaturated phosphonate structure. However, the presence of dienyl phosphonates resulting from a palladium-catalyzed elimination from the 3-acetoxy-1-alkenyl phosphonates **6a** and **6c** under the reaction conditions[9] cannot be excluded.



Scheme 2.

Åkermark et al.[10] have reported the catalytic acetoxylation of cyclohexene with iron nitrate as reoxidant, and proposed a mechanism which relies on a Pd–NO species, which can be further oxidised to an active Pd–NO_2 complex by molecular oxygen. Similar trends were put forward to explain the palladium-catalyzed oxidation of olefins,[11] the epoxidation of cyclic alkenes,[12] and some other metal-catalyzed reactions.[13] Our reactions may proceed through a similar pathway, as outlined in Scheme 2. Thus, a palladium nitroso complex **A** might be formed and further oxidised to a palladium nitro species **B** responsible for the acetoxylation.

Following this model, the formation of **7** may be rationalized through an internal migration of the nitro group in complex **C**. A similar trend was already described in a related system.[11a]

The superiority of isopentyl nitrite over the benzoquinone/manganese dioxide system as reoxidant deserves some comments. As demonstrated by Bäckvall,[14] the (π-allyl) palladium complex involved in the closely related palladium-catalyzed 1,4-diacetoxylation of conjugated dienes incorporates the benzoquinone directly coordinated to the metal. We can reasonably assume that the intermediate for the acetoxylation of cyclic allyl phosphonates using the benzoquinone/MnO_2 system has a similar structure. The formation of this (π-allyl) palladium complex from a cyclic allyl phosphonate may be prevented due to the steric congestion created by the presence of benzoquinone. On the other hand, the easier formation of the (π-allyl) palladium complex **C**, incorporating only the smaller NO_2 group coordinated to the metal, may account for the higher reactivity.

In conclusion, we have shown that the palladium-catalyzed acetoxylation of cyclic allyl phosphonates can be performed efficiently through the use of isopentyl nitrite as reoxidant, the reaction being run under oxygen. The use of only 20 mol% of nitrite (with respect to the substrate) is sufficient, indicating that the reaction may proceed via a nitro–nitrosyl redox couple with oxygen being the final oxidant. This procedure is attractive since it allows an easy dioxygen activation[15] and enables minimization of by-products, which is satisfactory from an environmental and economical point of view. We are currently applying this procedure to other organophosphorus substrates.

Experimental

All solvents were purified according to reported procedures, and reagents were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, on a Bruker AC 200 spectrometer working at 200.00 MHz and 50.16 MHz, respectively (the usual abbreviations are used: s: singulet, d: doublet, t: triplet, q: quadruplet, qt: quintuplet, o: octuplet, m: multiplet). Tetramethylsilane was used as internal standard.^{31}P NMR spectra were recorded on a Bruker AC 100 spectrometer at 40.54 MHz, using 85% H_3PO_4 as external standard. All chemical shifts are given in ppm. Infrared spectra (ν in cm^{-1}) were recorded as thin films on a Hewlett-Packard Paragon 1000. Elemental analyses

were carried out at the Microanalytical Center, Faculté de Saint Jérôme, Marseille. The starting cyclic allyl phosphonates were prepared by a Michaelis Becker[16] reaction from the corresponding dialkyl phosphites and the cyclic allyl bromides, which were in turn obtained via radical bromination of the cyclic alkenes with *N*-bromo succinimide and benzoyl peroxide in CCl_4.

General procedure for the palladium-catalyzed acetoxylation of cyclic allyl phosphonates

The reactions were run in a two necked round-bottomed flask fitted with a rubber septum and a condensor which was connected to a gas burette for the oxygen supply. In the flask were placed successively palladium chloride (17.7 mg, 0.1 mmol), potassium acetate (196 mg, 2 mmol), and the allyl phosphonate (1 mmol) in acetic acid (2 ml). The system was purged with oxygen by three vacuum/flushing cycles. Then isopentyl nitrite (200 μl, 1.5 mmol) was added via syringe, and the mixture was stirred at 60°C. The reaction was monitored by gas chromatography, or more simply, by measuring the oxygen uptake. After the end of the reaction, the mixture was cooled, diluted with ether (2×15 ml) and filtered over a short pad of Celite. The filtrate was washed with 10% Na_2CO_3, brine, and dried over $MgSO_4$. The residue obtained after filtration and removal of solvent was purified by flash chromatography over silicagel with ethyl acetate. ^1H and ^{13}C NMR data for acetoxy phosphonate **4b** were in full accordance with those already reported,[17] and ^{31}P NMR gives δ=19.7 ppm.

Diethyl (3-acetoxy cyclohexen-1-yl)phosphonate 4a. Colorless oil, R_f: 0.30 (ethyl acetate). [Found: C, 52.11; H, 7.56; P, 11.31. $C_{12}H_{21}O_5P$ requires: C, 52.17; H, 7.61; P, 11.23%]. IR (thin film): ν 1734 (C═O); 1641 (C═C); 1239 (P═O); 1164 (C–O); 1022 (P–O–C). ^1H NMR: 1.3 (t, C*H*$_3$CH$_2$O, $^3J_{HH}$=7.1 Hz); 1.5–2.2 (m, cyclic CH$_2$); 2.0 (s, C*H*$_3$C(O)); 4.0 (qt, CH$_3$C*H*$_2$O, $^3J_{HH}$=$^3J_{PH}$=7.1 Hz); 5.3 (m, C*H*–O); 6.5 (d, C*H*═C, $^3J_{PH}$=21.8 Hz). ^{13}C NMR: 16.3 (d, *C*H$_3$CH$_2$O, $^3J_{PC}$=6.5 Hz); 19.0 (d, CH$_2$, $^3J_{PC}$=11.2 Hz); 21.0 (s, *C*H$_3$C(O)); 24.2 (d, CH$_2$, $^2J_{PC}$=7.9 Hz); 27.4 (s, CH$_2$); 61.9 (d, CH$_3$*C*H$_2$O, $^2J_{PC}$=5.7 Hz); 67.5 (d, *C*H–O, $^3J_{PC}$=20.3 Hz); 132.6 (d, P–*C*═, $^1J_{PC}$=178.4 Hz); 139.0 (d, *C*H═C, $^2J_{PC}$=8.8 Hz); 170.0 (s, C═O). ^{31} P NMR: 17.1.

Di-isopropyl (3-acetoxy cyclohexen-1-yl)phosphonate 4c. Slightly yellow oil, R_f: 0.34 (ethyl acetate). [Found: C, 55.29; H, 8.18; P, 10.27. $C_{14}H_{25}O_5P$ requires: C, 55.26; H, 8.22; P, 10.20%]. IR (thin film): ν 1741 (C═O); 1615 (C═C); 1236 (P═O); 1161 (C–O); 1022 (P–O–C). ^1H NMR: 1.3 (d, (C*H*$_3$)$_2$CH–, $^3J_{HH}$=6.3 Hz); 1.6–2.3 (m, cyclic CH$_2$); 2.0 (s, C*H*$_3$C(O)); 4.7 (2o, (CH$_3$)$_2$C*H*–O, $^3J_{HH}$=$^3J_{PH}$=6.2 Hz); 5.3 (m, C*H*–O); 6.6 (d, C*H*═C, $^3J_{PH}$=21.9 Hz).^{13}C NMR: 19.2 (d, CH$_2$, $^3J_{PC}$=10.3 Hz); 21.0 (s, *C*H$_3$C(O)); 23.8 and 24.0 (d, (*C*H$_3$)$_2$CH, $^3J_{PC}$=4.1 Hz and $^3J_{PC}$=3.9 Hz); 24.2 (d, CH$_2$, $^2J_{PC}$= 8.6 Hz); 27.5 (s, CH$_2$); 67.6 (d, *C*H–O, $^3J_{PC}$=20.3 Hz); 70.6 (d, *C*H–O–P, $^2J_{PC}$=5.6 Hz); 133.8 (d, P–*C*═, $^1J_{PC}$=179.0 Hz); 138.4 (d, *C*H═C, $^2J_{PC}$=9.1 Hz); 170.3 (s, C═O). ^{31}P NMR: 14.9.

Diethyl (3-acetoxy cyclopenten-1-yl)phosphonate 5a. Colorless oil, R_f: 0.47 (ethyl acetate). [Found: C, 50.31; H, 7.31; P, 11.80. $C_{11}H_{19}O_5P$ requires: C, 50.38; H, 7.25; P, 11.83%]. IR (thin film): ν 1734 (C═O); 1617 (C═C); 1241 (P═O); 1163 (C–O); 1024 (P–O–C). ^1H NMR: 1.3 (t, C*H*$_3$CH$_2$O, $^3J_{HH}$=7.1 Hz); 1.8–2.7 (m, cyclic CH$_2$); 2.0 (s, C*H*$_3$C(O)); 4.1 (qt, CH$_3$C*H*$_2$O, $^3J_{HH}$=$^3J_{PH}$=7.1 Hz); 5.6 (m, C*H*–O); 6.5 (d, C*H*═C, $^3J_{PH}$=17.9 Hz). ^{13}C NMR: 16.2 (2d, *C*H$_3$CH$_2$O, $^3J_{PC}$=7.0 Hz); 20.8 (s, *C*H$_3$C(O)); 30.5 (d, CH$_2$, $^2J_{PC}$=10.4 Hz); 31.8 (d, CH$_2$, $^3J_{PC}$=12.8 Hz); 62.3 and 63.7(d, CH$_3$*C*H$_2$O, $^2J_{PC}$=5.8 Hz and $^2J_{PC}$=5.8 Hz); 80.0 (d, *C*H–O, $^3J_{PC}$=24.1 Hz); 137.2 (d, P–*C*═, $^1J_{PC}$=186.9 Hz); 143.1 (d, *C*H═C, $^2J_{PC}$=13.8 Hz); 170.7 (s, C═O). ^{31}P NMR: 13.7.

Diethyl (3-acetoxy cyclohepten-1-yl)phosphonate 6a. Colorless oil, R_f: 0.38 (ethyl acetate). [Found: C, 53.73; H, 7.90; P, 10.64. $C_{13}H_{23}O_5P$ requires: C, 53.79; H, 7.93; P, 10.69%]. IR (thin film): ν 1738 (C═O); 1645 (C═C); 1242 (P═O); 1163 (C–O); 1026 (P–O–C). ^1H NMR: 1.2 (2t, C*H*$_3$CH$_2$O, $^3J_{HH}$=7.0 Hz); 1.4–2.4 (m, cyclic CH$_2$); 2.0 (s, C*H*$_3$C(O)); 4.0 (2 qt, CH$_3$C*H*$_2$O, $^3J_{HH}$=$^3J_{PH}$=7.1 Hz); 5.4 (m, C*H*–O); 6.7 (d, C*H*═C, $^3J_{PH}$=24.6 Hz). ^{13}C NMR: 16.5 (d, *C*H$_3$CH$_2$O, $^3J_{PC}$=6.5 Hz); 21.3 (s, *C*H$_3$C(O); 26.0 (d, CH$_2$, $^3J_{PC}$=6.9 Hz); 27.8 (s, CH$_2$); 28.3 (d, CH$_2$, $^2J_{PC}$=8.9 Hz); 32.3 (d, CH$_2$, $^4J_{PC}$=2.4 Hz); 62.5 (d, CH$_3$*C*H$_2$O, $^2J_{PC}$=5.8 Hz); 74.8 (d, *C*H–O, $^3J_{PC}$=27.4 Hz); 131.8 (d, P–*C*═, $^1J_{PC}$=179.8 Hz); 150.9 (d, *C*H═C, $^2J_{PC}$=10.5 Hz); 176.7 (s, C═O). ^{31}P NMR: 19.5.

Di-isopropyl (3-acetoxy cyclohepten-1-yl)phosphonate 6c. Slightly yellow oil, R_f: 0.54 (ethyl acetate). [Found: C, 56.64; H, 8.55; P, 9.79. $C_{15}H_{27}O_5P$ requires: C, 56.60; H, 8.49; P, 9.75%]. IR (thin film): ν 1738 (C═O); 1615 (C═C); 1242 (P═O); 1168 (C–O); 1035 (P–O–C).^1H NMR: 1.3 (d, (C*H*$_3$)CH–, $^3J_{HH}$=6.1 Hz); 1.4–2.3 (m, cyclic CH$_2$); 2.0 (s, C*H*$_3$C(O)); 4.5 (o, (CH$_3$)C*H*–, $^3J_{HH}$= $^3J_{PH}$=6.2 Hz); 5.4 (m, C*H*–O); 6.6 (d, C*H*═C, $^3J_{PH}$= 24.9 Hz). ^{13}C NMR: 21.2 (s, *C*H$_3$C(O)); 23.7 (d, (*C*H$_3$)CH–, $^3J_{PC}$=4.6 Hz);26.7 (d, CH$_2$, $^3J_{PC}$=7.3 Hz); 27.6 (s, CH$_2$); 28.4 (d, CH$_2$, $^2J_{PC}$=10.1 Hz); 32.1 (s, CH$_2$); 72.0 (d, (CH$_3$)*C*H–, $^2J_{PC}$=5.9 Hz); 74.3 (d, *C*H–O, $^3J_{PC}$=27.0 Hz); 134.3 (d, P–*C*═, $^1J_{PC}$=176.1 Hz); 148.8 (d, P–C═*C*, $^2J_{PC}$=10.9 Hz); 170.2 (s, C═O). ^{31} P NMR: 17.1.

Di-isopropyl (3-nitro cyclohexen-1-yl)phosphonate 7 was isolated during purification of 4c. Yellow oil, R_f: 0.38 (ethyl acetate). IR (thin film): ν 1630 (C═C); 1540 and 1395 (NO$_2$); 1258 (P═O); 1014 (P–O–C).^1H NMR: 1.3 (d, (C*H*$_3$)$_2$CH–, $^3J_{HH}$=6.9 Hz); 1.7–2.4 (m, cyclic CH$_2$); 4.7 (o, (CH$_3$)$_2$C*H*–O, $^3J_{HH}$=$^3J_{PH}$=6.3 Hz); 5.5 (m, C*H*–NO$_2$); 6.6 (d, C*H*═C, $^3J_{PH}$=19.6 Hz).^{13}C NMR: 18.5 (d, CH$_2$, $^3J_{PC}$=10.1 Hz); 24.0 (s, (*C*H$_3$)$_2$CH), $^3J_{PC}$=4.3 Hz); 24.3 (d, CH$_2$, $^2J_{PC}$=7.6 Hz); 26.1 (s, CH$_2$); 70.9 (d, *C*H–O–P, $^2J_{PC}$=5.4 Hz); 76.4(d, *C*H–NO$_2$, $^3J_{PC}$=21.2 Hz);133.4 (d, *C*H═C, $^2J_{PC}$=10.2 Hz); 137.9(d, P–*C*═, $^1J_{PC}$=178.9 Hz). ^{31} P NMR: 13.6.

Acknowledgements

Financial support from Centre National de la Recherche Scientifique and Conseil Régional PACA as a grant to M.A. is gratefully acknowledged. We also acknowledge

financial support from 'Société de Secours des Amis des Sciences'.

References

1. (a) Heumann, A.; Åkermark, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 453–454. (b) McMurry, J. E.; Kocovsky, P. *Tetrahedron Lett.* **1984**, *25*, 4187–4190. (c) Muzart, J. *Bull. Soc. Chim. Fr.* **1986**, 65–77. (d) Hansson, S.; Heumann, A.; Rein, T.; Åkermark, B. *J. Org. Chem.* **1990**, *55*, 975–984. (e) Heumann, A., Jens, J. K., Réglier, M. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley, *42*, **1994**; p 483. (f) Grennberg, H., Bäckvall, J. E. *Transition Metals for Fine Chemicals and Organic Synthesis*; Bolm, C., Beller, M., Eds.; VCH: Weinheim, 1998.

2. (a) Frost, G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089–1122. (b) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, 1995; pp 290–422. (c) Malleron, J. L.; Fiaud, J. C.; Legros, J. Y. *Handbook of Palladium-Catalyzed Organic Reactions*; Academic Press, **1997**; pp 147–170.

3. Principato, B.; Maffei, M.; Siv, C.; Buono, G.; Peiffer, G. *Tetrahedron* **1996**, *52*, 2087–2096.

4. Attolini, M.; Maffei, M.; Principato, B.; Peiffer, G. *Synlett* **1997**, 384–386.

5. (a) Yokomatsu, T.; Shimizu, T.; Yuasa Y.; Shibuya, S. *Synlett*, **1995**, 1280–1282. (b) Lau, W. Y.; Zhang, L.; Wang, J.; Cheng, D.; Zhao, K. *Tetrahedron Lett.* **1996**, *37*, 4297–4300.

6. Nelson, A.; Warren, S. *Tetrahedron Lett.* **1996**, *37*, 1501–1504.

7. Tsuji, J.; Sakai, K.; Nagashima, H.; Shimizu, I. *Tetrahedron Lett.* **1981**, *22*, 131–134.

8. A similar isomerization process was reported for the acetoxylation of β,γ-unsaturated esters, see Ref. 7.

9. We have already reported an analoguous reaction during the palladium-catalyzed acetoxylation of (2-butenyl)-*tert*-butyl-phenyl phosphine oxide, see: Attolini, M.; Principato, B.; Peiffer, G.; Maffei, M. *Phosphorus, Sulfur, Silicon* **1998**, *142*, 229–238.

10. Larsson, E. M.; Åkermark, B. *Tetrahedron Lett.* **1993**, *34*, 2523–2526.

11. (a) Andrews, M. A; Kelly, K. P. *J. Am Chem. Soc.* **1981**, *103*, 2894–2896. (b) Bäckvall, J. E.; Heumann, A. *J. Am. Chem. Soc.* **1986**, *108*, 7107–7108. (c) Wenzel, T. T. *J. Chem. Soc., Chem. Commun.* **1989**, 932–933.

12. (a) Andrews, M. A.; Cheng, C. F. F. *J. Am Chem. Soc.*, **1982**, *104*, 4268–4270. (b) Chauvet, F.; Heumann, A.; Waegell, B. *J. Org. Chem.* **1987**, *52*, 1916–1922.

13. (a) Ugo, R.; Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Pickard, A.; Ben-Taarit, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 694–695. (b) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am Chem. Soc.* **1979**, *101*, 270–272.(c) Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am Chem. Soc.* **1980**, *102*, 6618–6619.

14. Bäckvall, J. E.; Gogoll, A. *Tetrahedron Lett.* **1988**, *29*, 2243–2246.

15. The problem of dioxygen activation for aerobic palladium-catalyzed acetoxylations or diacetoxylations has received attention from several research groups: (a) For the first successful allylic acetoxylation of cyclic olefins using molecular oxygen, see: Bäckvall, J. E.; Hopkins, R. B.; Grennberg, H.; Mader, M. M.; Awasthi, A. K. *J. Am Chem. Soc.*, **1990**, *112*, 5160–5166. (b) Grennberg, H.; Bergstad, K.; Bäckvall, J. E. *J. Mol. Catal. A* **1996**, *113*, 355–358 and references cited therein. (c) Yokota, T.; Fujibayashi, S.; Nishiyama, Y.; Sakaguchi, S.; Ishii, Y. *J. Mol. Catal. A* **1996**, *114*, 113–122. (d) Wöltinger, J.; Bäckvall, J. E.; Zsigmond, A. *Chem. Eur. J.* **1999**, *5*, 1460–1467.

16. Worms, K. H.; Schmidt-Dunker, M. In *Organic Phosphorus Compounds*, Kosolapoff, G. M., Maier, L. Eds.; Wiley: New York, 1976; 7 Chapter 18.

17. Öhler, E.; Zbiral, E. *Chem. Ber.* **1991**, *124*, 175–184.