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Hydrogenation of α-Oxophosphonates with Molecular Hydrogen Catalyzed by Palladium on Carbon Carrier as Synthesis Procedure for α-Hydroxyphosphonates

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Abstract—Hydrogenation with molecular hydrogen of substituted benzoylphosphonic acids ethyl esters provides a convenient preparation method for diethyl [hydroxy(aryl)methyl]phosphonates. Both the palladium on activated carbon and the palladium immobilized in a chitosan matrix applied on a carbon carrier sibunit can be employed as catalysts.

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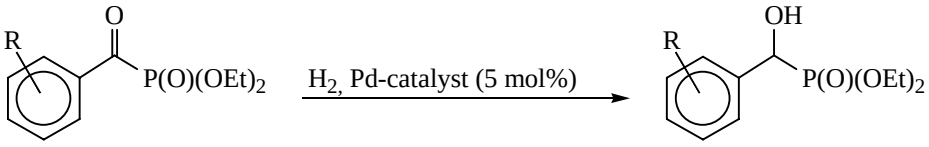
α-Hydroxyphosphonates are extensively studied first of all due to their probable application as drugs and bioregulators [1]. The basic synthetic procedures for α-hydroxyphosphonates are the hydrophosphonylation of carbonyl compounds (Abramov reaction) [2] and the reduction of available α-oxophosphonates [3]. The reduction of diethyl α-benzoylphosphonate in [4] was performed with sodium amalgam in aqueous-alcoholic solution of acetic acid. Further mostly boron hydrides were used as reductants: lithium triethylborodeuteride [5], and sodium borohydride [6–10]. At the use of a complex of $NaBH_4$ with *L*-(+)-tartaric acid [11] or of an optically active chloroborane containing pinane residue [12] the reduction the α-oxophosphonates occurred stereoselectively. An asymmetric catalytic reduction was achieved with the help of catecholborane in the presence of (*S*)-2-butyl-5,5-diphenyl-3,4-propano-1,3,2-oxazaborolidine [13–15].

No published data existed on the catalytic hydrogenation of α-oxophosphonates with molecular hydrogen (only unsuccessful attempt on hydrogenation in the presence of Raney nickel was mentioned [16]). Presumably this gap is due to the lability of the α-oxophosphonates in the presence of transition metal complexes [17] and also to the ready rupture of the P–C bond of the α-hydroxyphosphonates through a retro-Abramov reaction or a phosphonate-phosphate rearrangement (see, e.g., [16, 18, 19]). Whereas the hydrogenation of β-oxophosphonates was well known and was used, in particular, in the preparation of optically active β-hydroxyphosphonates [20–22], to the synthesis of the α-hydroxyphosphonates the hydrogenation with molecular hydrogen was applied only in the case of prochiral α,β-unsaturated precursors, 1-benzoyloxyalkenylphosphonates (O-benzoylated enol form) [23–25]. We believed that it was interesting to estimate the possibility to subject the α-oxophosphonates to the hydrogenation with molecular hydrogen; a commercially available palladium on carbon and also a palladium immobilized on chitosan matrix applied on a carbon carrier sibunit were chosen for catalysts.



Ia–Id **IIa–IId**

R = H (**a**), 4-Me (**b**), 2-Me (**c**), 4-MeO (**d**).

Hydrogenation of diethyl aroylphosphonates with hydrogen in the presence of palladium catalysts

Run no.	Initial compound	Pd-catalyst	Solvent	Pressure, at	Temperature, °C	Reaction time, h	Conversion, %	Yield of compound **II**, %
1	**Ia**	10%Pd/C	MeOH	1	65	1.5	100	96
2	**Ia**	10%Pd/C	MeOH	1	20	1	92	81
3	**Ib**	10%Pd/C	MeOH	1	65	2	100	99
4	**Id**	10%Pd/C	MeOH	1	65	1	100	95
5	**Ic**	10%Pd/C	MeOH	1	65	1	55	7
6	**Ic**	10%Pd/C	MeOH	10	20	6	100	100
7	**Ia**	1%Pd/chitosan/sibunit	EtOH	1	78	3	100	89
8	**Ia**	3%Pd/chitosan/sibunit	EtOH	1	78	3	85	57
9	**Ib**	1%Pd/chitosan/sibunit	EtOH	1	78	3	90	78
10	**Id**	1%Pd/chitosan/sibunit	EtOH	1	78	3	75	72
11	**Ic**	1%Pd/chitosan/sibunit	EtOH	1	78	3	62	53
12	**Ic**	1%Pd/chitosan/sibunit	MεOH	10	20	6	81	72

We selected for model compounds diethyl esters of benzoylphosphonic acids substituted in the ring **Ia–Id** and diethyl acetylphosphonate (**Ie**). The reactions were carried out in methanol or ethanol at the hydrogen pressure 1 at. The reaction progress was monitored by $^{31}P\{H\}$ NMR following the disappearance of the signal of the initial α-oxophosphonate **I** at δ –2.7÷–0.5 ppm and the accumulation of the signal of α-hydroxyphosphonate **II** at δ 21.8–22.5 ppm. The results obtained presented in the table show that in the presence of 5 mol% of 10% Pd on carbon diethyl benzoylphosphonate (**Ia**) is easily hydrogenated with hydrogen in the boiling methanol: at 100% conversion the yield of diethyl [hydroxy(phenyl)methyl]phosphonate (**IIa**) reaches 96% in 1.5 h (run no. *1*). In the reaction at the room temperature the conversion within 1 h was 92%, but the selectivity of the process considerably reduced, and the yield of the target product was but 81% (run no. *2*).

Introduction of donor substituents into the aromatic ring of benzoylphosphonate is known [18] to decrease its tendency to reduction; however, in the presence of 10%Pd/C substrates **Ib** and **Id** containing methyl and methoxy substituents in the *para*-position are hydrogenated as readily as **Ia** giving the corresponding α-hydroxyphosphonates **IIa** and **IIb** in nearly quantitative yield (runs nos. *3* and *4*).

We met difficulties in hydrogenation of the sterically hindered substrate **Ic** containing an *ortho*-methyl substitutent. In boiling methanol the conversion of compound **Ic** within 1 h attained 55%, and the yield of α-hydroxyphosphonate **IIc**, 7%; among the other reaction products appeared diethyl (19%), dimethyl (5%), and mixed (3%) phosphites (run no. *5*). Nearly the same results were obtained on replacing methanol by higher boiling ethanol. We succeeded to obtain α-hydroxyphosphonate **IIc** in quantitative yield by increasing the hydrogen pressure to 10 at (run no. *6*). We believe that the considerable decrease in selectivity at the hydrogenation of α-oxophosphonate **Ic** on 10%Pd/C at the atmospheric pressure is caused by diffusion limitations which are removed in the reaction carried out at higher pressure.

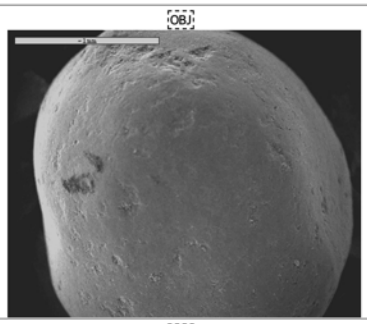
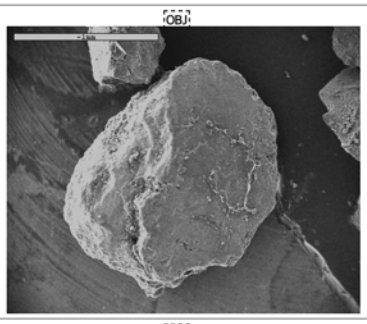
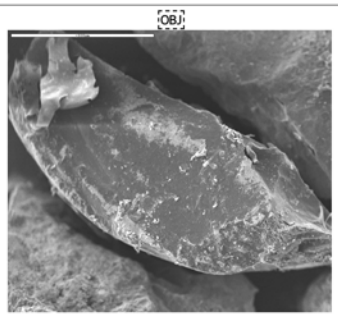
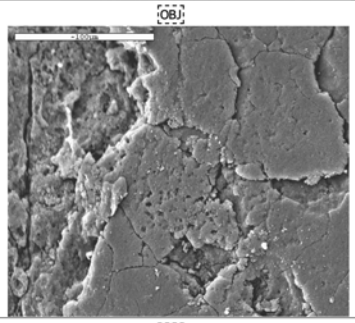
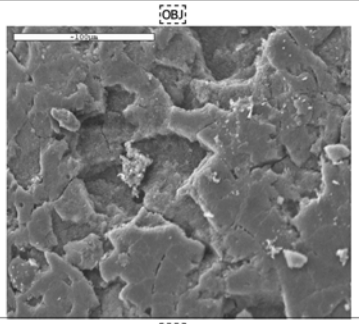
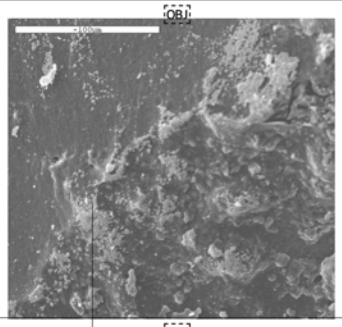
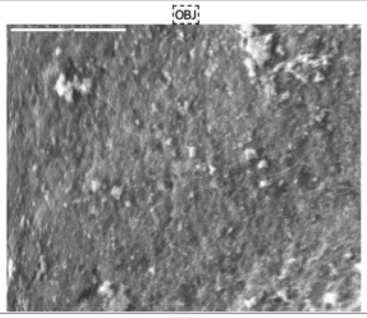
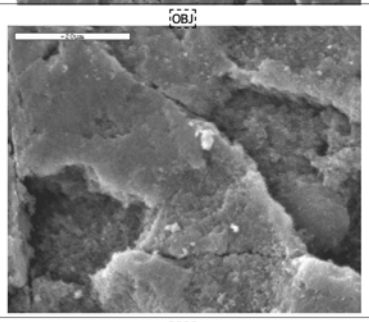
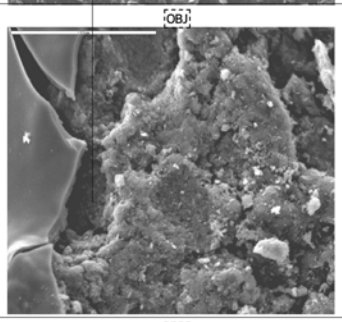
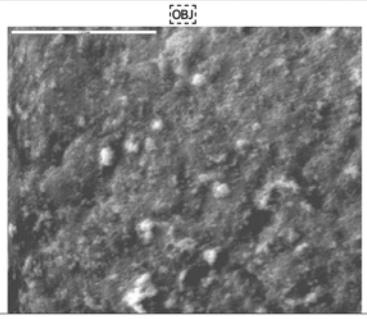
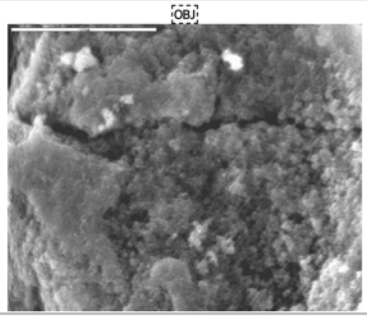
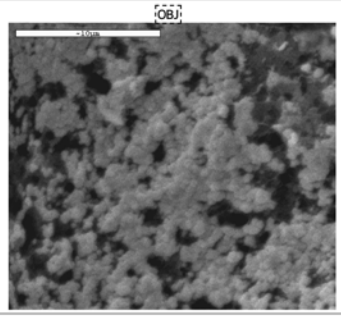
The hydrogenation rate at the use of palladium catalyst based on chitosan applied on sibunit (Pd/chitosan/sibunit) proved to be somewhat lower that that for 10%Pd/C (cf. runs nos. *1* and *7*). At the palladium content in the sample of 1 wt% the quantitative conversion of α-oxophosphonate **Ia** in the presence of 5 mol% of 1%Pd/chitosan/sibunit was reached within 3 h in boiling ethanol; therewith the yield of the target product **IIa** was 89% (run no. *7*). The replacement of methanol by ethanol in this case was due to low reproducibility of results obtained in MeOH (by yet unknown reasons).

The increase in the palladium concentration on the carrier from 1 to 3 wt% resulted in considerable reduction in the catalyst activity: under the same conditions the conversion and yield diminished to 85 and 57% respectively (run no. *8*). The investigation of the samples of Pd/chitosan/sibunit by scanning electron microscopy revealed (see the figure) that unlike the systems based on silica gel [26] the chitosan unevenly covered the sibunit surface. It is presumably caused by the hydrophobicity of the surface of sibunit that is a carbon carrier,

whereas the silica gel is hydrophilic. 2000-Fold magnification clearly shows that the polymer coats the sibunit surface unevenly, with cracks, and this fact is especially obvious for the sample containing 3 wt% of palladium and consequently larger amount of the polymer. In this catalyst at 5000-fold magnification separate isles of palladium/chitosan complex are visible. We presume that this nonuniformity results in formation of at least two types of catalytic centers: heterogeneous, namely, Pd on sibunit, and heterogenized, Pd immobilized in a chitosan matrix applied on sibunit surface.

In the presence of 1%Pd/chitosan/sibunit the decelerating effect of electon-donor groups is revealed: the hydrogenation rate of α-oxophosphonate **Ib** (see the table, run no. *9*) and especially **Id** (run no. *10*) are

Results of investigation of surface of sibunit and samples Pd/chitosan/sibunit with alternating palladium content by scanning electron microscopy

Magnification	Sibunit	1%Pd/chitosan/sibunit	3%Pd/chitosan/sibunit
×50			
×500			
× 2000			
×5000			

considerably reduced, although the selectivity of the process is not notably affected. In contrast, the sterical factor at the use of 1%Pd/chitosan/sibunit is not so important as with 10%Pd/C. The hydrogenation rate in going from 4-methyl-substituted α-oxophosphonate **Ib** (run no. *9*) to 2-methyl-substituted α-oxophosphonate **Ic** (run no. *11*) decreases, but not as significantly as at the use of palladium on carbon (cf. runs nos. *3* and *5*). Presumably the observed reduced sensitivity to the steric factor in the system 1%Pd/chitosan/sibunit is due to the above mentioned presence on the catalyst surface of two types of active centers. Probably in the hydrogenation reaction on the second type heterogenized centers the diffusion limitations are not as severe as in the system 10%Pd/C.

Our attempt to replace the carbon carriers by silica gel failed. We formerly demonstrated [26] that a three-component palladium-containing system based on chitosan applied on silica gel and modified with glutaric aldehyde exhibited a high catalytic activity in hydrogenation (also chemoselective) of α,β-unsaturated phosphonic acids and their esters. With α-oxophosphonate **Ia** the application of this catalyst resulted in decomposition with the formation of diethyl phosphite.

Unlike aromatic α-oxophosphonates **Ia–Id** aliphatic diethyl acetylphosphonate (**Ie**) did not undergo hydrogenation in the boiling methanol either in the presence of the palladium on carbon or on sibunit; the main reaction product was diethyl phosphite containing a small amount of dimethyl and methylethyl phosphates. The formation of diethyl (1-hydroxyethyl)phosphonate (**IIe**) was detected only in reaction performed at room temperature; in the presence of 10%Pd/C at 75% conversion of compound **Ie** after 1 h the yield of compound **IIe** was 11%, that of diethyl phosphite 64%.

Thus we demonstrated that unlike aliphatic α-oxophosphonates the hydrogenation of benzoylphosphonic acids esters can be a convenient method of preparation of [hydroxy(aryl)methyl]-phosphonates. As the hydrogenation catalyst may be used both palladium on the activated carbon and that immobilized in a chitosan matrix applied on carbon carrier sibunit.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P{H} NMR spectra were registered on a spectrometer Bruker Avance-400 at operating frequencies 400, 101, and 162 MHz respectively. The chemical shifts were measured in ^{31}P{H} NMR spectra from an external reference 85% H_3PO_4, in ^{1}H NMR spectra, from internal reference TMS, and in ^{13}C NMR spectra, from the solvent signal ($CDCl_3$ 77.0 ppm, CD_3OD 49.0 ppm). The microphoto of catalyst samples were obtained using scanning microscope JSM-5300LV JEOL. A thin layer of gold was applied on the sample surface on a JFC-1100E instrument. Methanol and ethanol were boiled and distilled over magnesium methylate and calcium ethylate respectively. Palladium on carbon (10%Pd/C) was purchased from Aldrich.

1%Pd/chitosan/sibunit. Sibunit (7 g, fraction 0.63–1.00 mm, S_{BET} 300 m^2/g, moisture capacity 1.0 ml/g) was impregnated with 7.0 ml of chitosan solution in 1% aqueous acetic acid (chitosan content in the solution 8 g/l). After drying in air the sibunit sample coated with chitosan was treated with 0.105 ml of 50% water solution of glutaric aldehyde in 20 ml of MeOH for 1 h (calculated degree of crosslinking 10%). Then the sample was washed with MeOH and dried in air. The treatment of sibunit with chitosan and glutaric aldehyde was performed three times in succession. Thus prepared system chitosan/sibunit was treated with a solution of 0.194 g of Na_2PdCl_4 in 15 ml of H_2O. Palladium-containing sample was washed with water and MeOH, dried in air, and then in a vacuum-desiccator over P_2O_5.

3%Pd/chitosan/sibunit was prepared in a similar way. The treatment of sibunit with chitosan and glutaric aldehyde was performed nine times in succession. Palladium was applied from a solution of 0.582 g of Na_2PdCl_4 in 20 ml of H_2O.

α-Oxophosphonates Ia–Ie were prepared by standard procedures [4, 27–29] and purified by distillation; their spectral characteristics are given below.

Diethyl benzoylphosphonate (Ia) [4, 27], bp. 145°C (2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 d.t (6H, CH_3, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5 Hz), 4.29 m (4H, CH_2), 7.52 m (2H$_{arom}$), 7.64 t.t (1H$_{arom}$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.3 Hz), 8.28 m (2H$_{arom}$). ^{31}P{H} NMR spectrum ($CDCl_3$), δ, ppm: –1.1.

Diethyl (4-methylbenzoyl)phosphonate (Ib), bp 155°C (2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (6H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.2 Hz), 2.42 s (3H, CH_3Ph), 4.28 m (4H, CH_2), 7.31 d (2H$_{arom}$, $^3J_{HH}$ 7.9 Hz), 8.18 d (2H$_{arom}$, $^3J_{HH}$ 7.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.26 (CH_3, $^3J_{PC}$ 5.9 Hz), 63.93 (CH_2, $^2J_{PC}$ 7.6 Hz), 128.75 (2CH$_{arom}$), 129.73 (2CH$_{arom}$), 134.67 (CH$_{arom}$), 135.44 (C$_{arom}$, $^2J_{PC}$ 64.1 Hz), 198.86 (CO, $^1J_{PC}$ 175.4 Hz). ^{31}P{H} NMR spectrum ($CDCl_3$), δ, ppm: –0.9.

Diethyl (2-methylbenzoyl)phosphonate (Ic), bp 126–130°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (6H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 2.54 s (3H, CH_3Ph), 4.27 m (4H, CH_2), 7.28 d (1H$_{arom}$, $^3J_{HH}$ 7.2 Hz), 7.35 t (1H$_{arom}$), 7.46 t (1H$_{arom}$), 8.46 d (1H$_{arom}$, $^3J_{HH}$ 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.13 (C$\underline{H}_3$CH$_2$, $^3J_{PC}$ 5.1 Hz), 21.62 (CH_3Ph), 63.61 (CH_2, $^2J_{PC}$ 7.3 Hz), 129.34 (2CH$_{arom}$), 129.75 (2CH$_{arom}$), 133.16 (C$_{arom}$, $^2J_{PC}$ 64.4 Hz), 145.79 (C$_{arom}$), 198.07 (CO, $^1J_{PC}$ 173.8 Hz). ^{31}P{H} NMR spectrum ($CDCl_3$), δ, ppm: –1.2.

Diethyl (4-methoxybenzoyl)phosphonate (Id) [27, 28]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (6H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 3.89 s (3H, CH_3O), 4.27 m (4H, CH_2), 6.98 d (2H$_{arom}$, $^3J_{HH}$ 8.8 Hz), 8.29 d (2H$_{arom}$, $^3J_{HH}$ 8.8 Hz). ^{13}C NMR spectrum ($CDCl)_3$, δ, ppm: 16.16 (C$\underline{H}_3$CH$_2$, $^3J_{PC}$ 5.9 Hz), 55.42 (CH_3O), 63.62 (CH_2, $^2J_{PC}$ 6.7 Hz), 63.22 (CH_2, $^2J_{PC}$ 6.7 Hz), 113.95 (2CH$_{arom}$), 128.78 (C$_{arom}$, $^2J_{PC}$ 64.9 Hz), 132.29 (2CH$_{arom}$), 164.73 (C$_{arom}$), 196.34 (CO, $^1J_{PC}$ 173.7 Hz). ^{31}P{H} NMR spectrum ($CDCl_3$), δ, ppm: –0.5.

Diethyl acetylphosphonate (Ie) [29], bp. 96–99°C (12 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (6H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 2.49 d (3H, CH_3CO, $^3J_{PH}$ 5.2 Hz), 4.21 m (4H, CH_2). ^{31}P{H} NMR spectrum ($CDCl_3$), δ, ppm: –2.7.

Diethyl [hydroxy(phenyl)methyl]phosphonate (IIa) [4, 5, 13, 30]. Into a flask equipped with a magnetic stirrer, a reflux condenser with a Wuertz adapter, a long capillary going through the condenser to the bottom of the flask, and a bubbler was charged 0.05 g (0.2 mmol) of compound **Ia** in 4 ml of anhydrous methanol. The device was filled with argon through the capillary, and 0.01 g (5 mol%) of 10%Pd/C was charged thereto. The argon flow was stopped, and through the same capillary the device was flushed with hydrogen. The reaction mixture was heated at reflux for 1 h under a constant flow of hydrogen while stirring, then it was cooled, the catalyst was filtered off through a thin bed of silica gel, and the solvent was distilled off on a rotary evaporator. The residue was dissolved in CD_3OD and subjected to spectral analyses. Yield according to the data of ^{31}P{H} NMR spectrum was 96%. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.22 t (3H, CH_3, $^3J_{HH}$ 7.1 Hz), 1.26 d.t (3H, CH_3, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5 Hz), 3.95–4.10 m (4H, CH_2), 4.80 s (1H, OH), 5.00 d (1H, CHP, $^2J_{HP}$ 12.9 Hz), 7.29 m (1H$_{arom}$), 7.35 m (2H$_{arom}$), 7.48 m (2H$_{arom}$). ^{13}C NMR spectrum (CD_3OD), δ, ppm: 16.66 (CH_3, $^3J_{PC}$ 5.9 Hz), 16.72 (CH_3, $^3J_{PC}$ 5.9 Hz), 64.24 (CH_2, $^2J_{PC}$ 7.3 Hz), 64.55 (CH_2, $^2J_{PC}$ 8.1 Hz), 71.44 (CHP, $^1J_{PC}$ 166.1 Hz), 128.58 (2CH$_{arom}$, $^3J_{PC}$ 5.1 Hz), 129.10 (CH$_{arom}$), 129.15 (2CH$_{arom}$), 138.70 (C$_{arom}$). ^{31}P NMR spectrum (CD_3OD), δ, ppm: 21.8.

Compounds **IIb** and **IId** were similarly obtained.

Diethyl [hydroxy(4-methylphenyl)methyl]phosphonate (IIb). Yield 99%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.20 t (3H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 1.26 t (3H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.0 Hz), 2.34 s (3H, CH_3Ph), 3.94–4.08 m (4H, CH_2), 4.96 d (1H, CHP, $^2J_{HP}$ 10.6 Hz), 7.15 d (2H$_{arom}$, $^2J_{HH}$ 7.8 Hz), 7.36 d.d (2H$_{arom}$, $^2J_{HH}$ 7.8, $^4J_{PH}$ 1.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.27 (C$\underline{H}_3$CH$_2$, $^3J_{PC}$ 3.6 Hz), 16.32 (C$\underline{H}_3$CH$_2$, $^3J_{PC}$ 5.0 Hz), 21.09 (CH_3Ph), 62.93 (CH_2, $^2J_{PC}$ 7.2 Hz), 63.18 (CH_2, $^2J_{PC}$ 7.2 Hz), 70.63 (CHP, $^1J_{PC}$ 160.3 Hz), 127.02 (2CH$_{arom}$, $^3J_{PC}$ 5.9 Hz), 128.88 (2CH$_{arom}$), 133.64 (C$_{arom}$), 137.68 (C$_{arom}$). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 22.0.

Diethyl hydroxy(4-methoxyphenyl)methyl]phosphonate (IId) [30, 31]. Yield 95%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 t (3H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 1.27 t (3H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 3.8 s (3H, CH_3O), 3.91–4.09 m (4H, CH_2), 4.95 d (1H, CHP, $^2J_{HP}$ 10.1 Hz), 6.88 d (2H$_{arom}$, $^2J_{HH}$ 8.7 Hz), 7.41 d.d (2H$_{arom}$, $^2J_{HH}$ 8.7, $^4J_{PH}$ 1.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.32 (C$\underline{H}_3$CH$_2$), 55.16 (CH_3O), 62.91 (CH_2, $^2J_{PC}$ 7.6 Hz) 63.22 (CH_2, $^2J_{PC}$ 6.7 Hz), 70.23 (CHP, $^1J_{PC}$ 161.0 Hz), 113.61 (2CH$_{arom}$), 128.41 (2CH$_{arom}$, $^3J_{PC}$ 6.8 Hz), 128.67 (C$_{arom}$), 159.37 (C$_{arom}$). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 22.1.

Diethyl hydroxy(2-methylphenyl)methyl]phosphonate (IIc). Into a steel pressure reactor with a glass lining equipped with a magnetic stirrer and flushed with dry argon was charged 0.056 g (0.2 mmol) of α-oxophosphonate **Ic** in 4 ml of anhydrous methanol and 0.011 g (5 mol%) of 10%Pd/C. The hydrogen pressure was raised to 10 at, and the reaction mixture was stirred at room temperature for 6 h. The catalyst was filtered off through a thin bed of silica gel, and the solvent was distilled off on a rotary evaporator. The residue was dissolved in $CDCl_3$and subjected to spectral analyses. Yield according to the data of ^{31}P{H} NMR spectrum was 100%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.20 t (3H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.0 Hz), 1.26 t (3H, C$\underline{H}_3$CH$_2$, $^3J_{HH}$ 7.0 Hz), 2.37 s (3H, CH_3Ph), 3.90–4.10 m (4H, CH_2), 4.50 br.s (1H, OH), 5.27 d (1H, CHP, $^2J_{HP}$ 10.9 Hz), 7.14 d (1H$_{arom}$, $^3J_{HH}$ 7.1 Hz), 7.22 m (2H$_{arom}$), 7.66 d (1H$_{arom}$, $^3J_{HH}$ 7.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16.26 (C$\underline{H}_3$CH$_2$, $^3J_{PC}$ 4.4 Hz), 16.31 (C$\underline{H}_3$CH$_2$, $^3J_{PC}$ 5.1 Hz), 19.48 (CH_3Ph), 62.88 (CH_2, $^2J_{PC}$ 7.3 Hz), 63.36 (CH_2, $^2J_{PC}$ 7.3 Hz), 67.02 (CHP, $^1J_{PC}$ 160.3 Hz), 126.01,

127.16, 127.85, 130.09 (CH_{arom}), 135.10 (C_{arom}), 135.67 (C_{arom}, $^2J_{PC}$ 6.6 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 22.5.

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