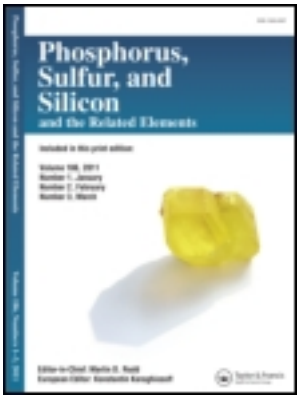

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INTERACTION OF TRIS(3-HYDROXYMETHYL)PHOSPHINE WITH CINNAMIC ACIDS

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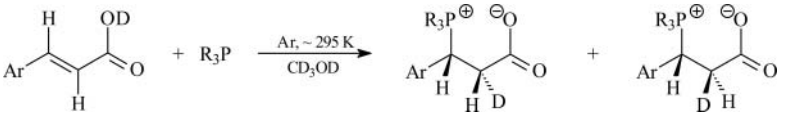
GRAPHICAL ABSTRACT



Abstract *Phosphonium zwitterions of the known type $R_3P^+CH(Ar)CH_2CO_2^-$ (**II**) are obtained as a racemic mixture in moderate yield via a 1:1 reaction of cinnamic acids (Ar = phenyl, or substituted phenyl) with $[HO(CH_2)_3]_3P$ in acetone at room temperature under Ar. The products are characterized by elemental analysis, $^{31}P\{^1H\}$-, ^1H-, and $^{13}C\{^1H\}$-NMR spectroscopies, and mass spectrometry, although they contain a minor coproduct formed via neutralization of the positive and negative charges of **II** with the respective acid and phosphine reactants (see Experimental Section). In CD_3OD, the monodeuterated salts $R_3P^+CH(Ar)CH(D)CO_2^-$ are formed as a mixture of diastereomers with d.r. values of ~2 to 8, depending on substituent groups present in the organic acid; in these studies, 2-HO-cinnamic acid is the most reactive, and β-methylcinnamic acid is the least reactive.*

Keywords (3-Hydroxypropyl)phosphine; cinnamic acids; phosphobetaine; diastereomeric ratio

INTRODUCTION

Investigations into transition metal-catalyzed hydrogenation of lignin and lignin model compounds[1] led to the discovery that water-soluble (hydroxyalkyl)phosphines (and their phosphonium salt precursors) are excellent bleaching and brightness stabilization agents for wood pulps.[2] Subsequent investigations have shown that this ability results from interaction of the nucleophilic phosphine with conjugated C=C−C=O moieties present within lignin chromophores,[3] and our group has reported on such phosphine interactions

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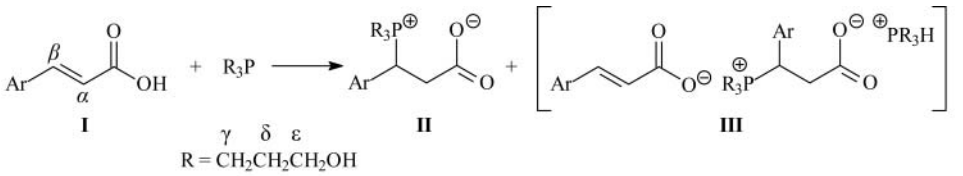
with aromatic aldehydes,[4] aromatic and cinnamic alcohols,[5] α,β-unsaturated aldehydes,[6] and quinones.[7]

This present work describes the interaction of $[HO(CH_2)_3]_3P$, i.e. tris(3-hydroxypropyl)phosphine, abbreviated as THPP, with cinnamic acids, which are precursors of monolignols that subsequently polymerize to lignins.[8] Our previous investigations have shown that THPP has less bleaching ability than tris(hydroxymethyl)phosphine $(HOCH_2)_3P$,[2] but is less prone to side-reactions that can complicate studies with the hydroxymethyl phosphine: the (α-hydroxy)phosphine tends to lose aldehyde with formation of the P–H functionality, which is reactive toward unsaturated organics.[6c,9,10]

Reactions of phosphines with α,β-unsaturated carbonyl compounds typically occur via nucleophilic attack of the phosphorus on the activated C=C bond, with formation of phosphabetaines (e.g., the **I** → **II** reaction of Scheme 1 discussed below). Examples include aqueous reactions of (m-$NaSO_3C_6H_4)_3P$ and (m-$NaSO_3C_6H_4)Ph_2P$ with acrylic, methacrylic, crotonic, and itaconic acids,[11] and reactions of Ph_3P with methacrylic, cinnamic, and p-methoxycinnamic acids in $CHCl_3$.[12] Kinetic and mechanistic details of the $PPh_3/\alpha,\beta$-unsaturated carboxylic acids systems in acetic acid, alcohol media, and aprotic solvents have recently been published.[13]



I II III

a, Ar = Ph; **b**, Ar = 2-HOC_6H_4; **c**, Ar = 3-HOC_6H_4; **d**, Ar = 4-HOC_6H_4 (*p*-coumaric acid); **e**, Ar = 3,4-$(MeO)_2C_6H_3$; **f**, Ar =4-OH-3-MeO-C_6H_3 (ferulic acid); **g**, Ar = 3,4-$(HO)_2C_6H_3$ (caffeic acid); **h**, Ar = 4-HO-3,5-$(MeO)_2C_6H_2$ (sinapic acid)

Scheme 1

RESULTS AND DISCUSSION

A 1:1 reaction of THPP with cinnamic acid (**Ia**) in acetone at room temperature (r.t., ~295 K) under Ar precipitated over 24 h a white, hygroscopic solid that is a mixture of two products. The major one is the zwitterionic phosphabetaine **IIa**, formed as a racemic mixture via nucleophilic attack of the phosphine at the β-C atom of **Ia** (Scheme 1). The $^{31}P\{^1H\}$ spectrum of the solid in D_2O revealed a singlet at $\delta_P = 38.3$, consistent with a phosphonium species[4,5,6a,b,d,7] such as **IIa**. The ^1H data (see Section Experimental) are consistent with the structure, with the α- and β-protons generating an MABX spin system that is well simulated (Figure 1). The γ-, δ- and ε-protons of the THPP moiety (multiplets centered at $\delta_H = 2.34, 1.77, 3.67$, respectively) are downfield-shifted of those of free THPP (multiplets at $\delta_H = 1.47, 1.63, 3.60$, respectively), and form the same pattern as those reported for other THPP-derived phosphonium salts.[4,5,6b,7] The β-C atom of **IIa** appears in the $^{13}C\{^1H\}$ spectrum as a doublet at $\delta_C = 37.7$ ($^1J_{PC} = 44$ Hz). The ESI-MS (in MeOH) shows the major peak corresponding to the protonated form of **IIa** and a minor peak due to protonated THPP. The elemental analysis of the mixture is consistent with the formulation of **II** because the coproduct (see below) is of the same formulation.

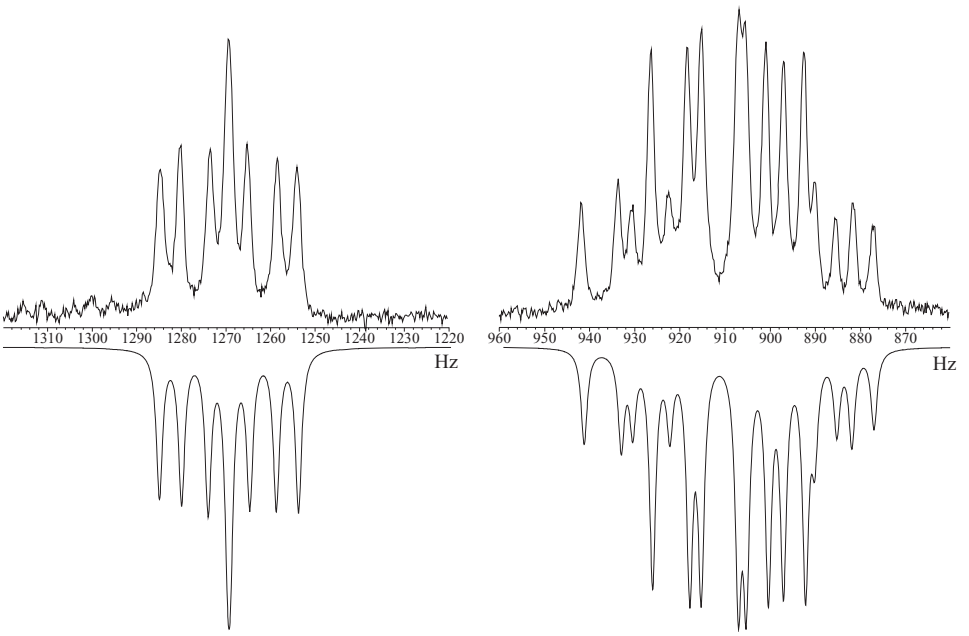
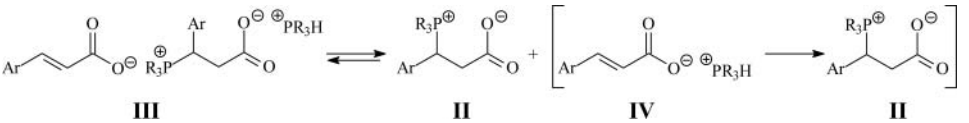


Figure 1 Experimental (top) and simulated (bottom) ^{1}H spectra for the α- and β-protons of **IIa** in D_2O; there is one MABX spin system with $^3J_{MA} = 11.4$, $^3J_{MB} = 4.3$, $^2J_{AB} = 15.7$, $^2J_{XM} = 15.0$, $^3J_{XA} = 8.0$, and $^3J_{XB} = 8.4$, where X is the P-atom; H_M, H_A, and H_B resonances at 1269.2, 922.7, and 893.3 Hz, respectively; spectral half-width = 1.8 Hz.

The minor product is thought to be the intermolecular phosphonium salt **IIIa** formed via neutralization of positive and negative charges of **IIa** with the anion of **Ia** and protonated THPP, respectively. **IIIa** is not detected in the solution NMR spectra because it decomposes into **IIa** and the reactants **Ia** and THPP, which then form the intermolecular phosphonium salt **IV** (Scheme 2), as judged by the ^{1}H-spectral data. Multiplets for the γ-, δ-, and ε-protons of the THPP moiety, which will be averaged signals due to proton exchange between the cinnamate and $THPPH^+$, are centered at $\delta_H = 2.45$, 1.95, 3.74, respectively, and are downfield-shifted from those of **IIa** and THPP; the α-H of **IV** is seen as a doublet at $\delta_H = 6.57$ ($^3J_{HH} = 16.2$ Hz) while the β-H is hidden by the Ph signals. The ^{1}H data show that **IV** is formed initially in 17% yield, but then slowly disappears due to conversion into **IIa** (Scheme 2).

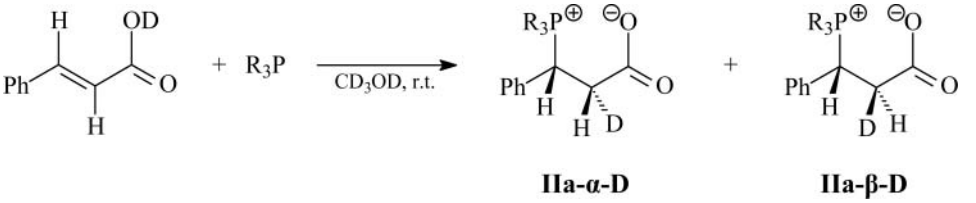


Scheme 2

Cinnamic acids **Ib–h** react similarly with THPP to afford **IIb–h**, and the corresponding byproduct **IIIb–h** again in ~15%–25% yield. The $^{31}P\{^1H\}$ shifts of **IIc–h** (δ_P = 38.3–38.0), and the ^{1}H and $^{13}C\{^1H\}$ resonances of the THPP and acid moieties, are similar to those of **IIa**. For **IIb**, formed from 2-HO-cinnamic acid, compared to these similar data,

the $^{31}P\{^{1}H\}$ singlet is at lower field ($\delta_P = 39.3$), the β-C atom is seen as a broad singlet (vs. a doublet) at a higher field ($\delta_C = 31.2$), and the β-proton appears as a broad triplet (vs. a ddd) at significantly lower field ($\delta_H = 4.60$). Such features of **IIb** are likely due to an *ortho*-effect of the HO-group of the aromatic ring, which could form a resonance structure with the phosphonium cation via a five-member cyclic ring.

A 1:1 reaction of **Ia** with THPP in CD_3OD ([THPP] = [**Ia**] = 0.1 mol/L, r.t., Ar) affords the monodeuterated salt **IIa–D** as a mixture of diastereomers (Scheme 3). Monitoring the reaction by the NMR spectrometry revealed the following features: immediately observed in the reaction mixture is a broad $^{31}P\{^{1}H\}$ singlet for the THPP species at $\delta_P = -25.6$, which is downfield-shifted from the sharp singlet of THPP ($\delta_P = -29.5$) recorded separately. [In H_2O, the $^{31}P\{^{1}H\}$ singlets vary with pH from δ_P –29.6 for THPP to +17.0 for $THPP^{+}H$ ($pK_a \sim 7.2$); broad signals at intermediate pH values result from averaging of these resonances due to fast proton exchange between the two species;[14] in CD_3OD, compared to the D_2O system, the $THPPH^{+}$/THPP equilibrium will favor more the neutral species and thus the $\delta_P = -25.6$ value seems appropriate for the equilibrium between these two species]. The respective $\delta_H = 6.49$ and 7.65 doublets of the α- and β-protons of **Ia** in the mixture are slightly upfield-shifted of those of **Ia** ($\delta_H = 6.48$ and 7.68) that were also recorded separately. These data indicate that an acid–base interaction of THPP and **Ia** in methanol first forms the intermediate species **IV**. Over hours (cf. see Figure 4 below), the broad $^{31}P\{^{1}H\}$ THPP singlet is replaced by a sharp singlet at $\delta_P = 38.7$ signal, corresponding to the P atom of **IIa–D**.

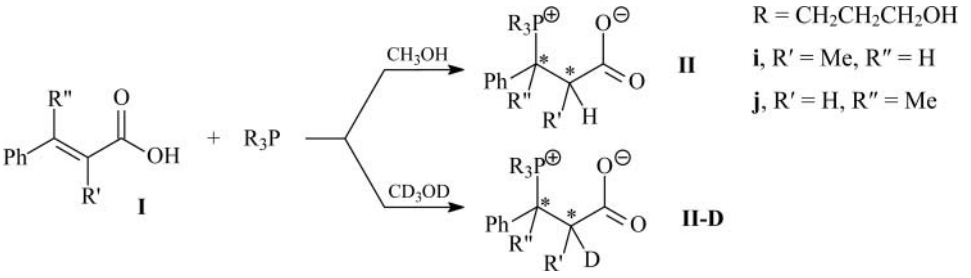


Scheme 3

The α- and β-protons of the two diastereomers of **IIa–D** appear in the ^{1}H spectrum as two overlapping three-spin systems that are readily simulated using a d.r. of ~2.0 (Figure 2). Formation of the corresponding monodeuterated stereoisomers was observed for all the cinnamic acids, and in most systems the d.r. was ~2. For **Ib** (2-HO-cinnamic acid), the ^{1}H patterns for the α- and β-protons of **IIb–D** (Figure 3) imply a d.r. value of ~5; the α- and β-protons of the major isomer appear as a doublets of doublets at $\delta_H = 2.96$ ($^{3}J_{HH} = 6.4$; $^{3}J_{PH} = 11.8$ Hz) and $\delta_H = 4.60$ ($^{3}J_{HH} = 6.4$; $^{2}J_{PH} = 15.4$ Hz), respectively.

The reaction rates of the cinnamic acids depend on substituents in the aromatic ring. Figure 4 illustrates consumption of the acids, according to integration values in the ^{1}H spectra, in a set of reactions ([THPP] = [acid] = 0.1 mol/L, CD_3OD, r.t., Ar). The reaction rates decrease in the order: **Ib** (2-HO-cinnamic acid) > **Ic** > **Ia** > **Ie** > **If** ≈ **Id** ≈ **Ig** ≈ **Ih**, the last four being naturally occurring cinnamic acids containing the 4-OH group.[8,15]

The r.t. reactions with α- and β-methylcinnamic acids (**Ii** and **Ij**, respectively) are very slow and required heating (Scheme 4). The isolated **IIi** and **IIj** products were viscous, and satisfactory elemental analyses were not obtained, C and H analyses were both ~0.7% higher than the calculated values. However, the NMR data are consistent with the formulations. An NMR-scale, 1:1 reaction of **Ii** in CD_3OD at 60°C was monitored by the



Scheme 4 [In IIj, the -carbon is a non-chiral centre with diastereomeric (anisochronous) protons]

$^{31}P\{^{1}H\}$ NMR and, after 7 days, 85% of THPP had reacted. The two diastereomers of the monodeuterated phosphobetaine **IIi–D** were seen at $\delta_P = 38.1$ and 37.6 with relative intensities 1.0:7.5, respectively. The ^{1}H doublet of the β-H ($\delta_H = 7.67$; $^{4}J_{HH} = 1.5$ Hz) of the reactant **Ii** was replaced by two overlapping doublets at $\delta_H = 3.92$ and 3.85 (ratio 1:8), which collapsed into singlets in the $^{1}H\{^{31}P\}$ spectrum ($^{2}J_{PH} \approx 15$ Hz); the Me resonance of **Ii** at $\delta_H = 2.08$ (d, $^{4}J_{HH} = 1.5$ Hz) was gradually replaced by a doublet at $\delta_H = 1.06$ ($^{4}J_{HH} = 1.2$ Hz) and a singlet at $\delta_H = 1.00$ in a respective ratio of 8:1.

The same reaction was carried out in MeOH in order to compare the ^{1}H NMR spectra of **IIi–D** and **IIi**. After 7 days of reaction at 60°C, the MeOH was removed in vacuo and the residue was redissolved in CD_3OD where it remains as **IIi**. Integration in the $^{31}P\{^{1}H\}$

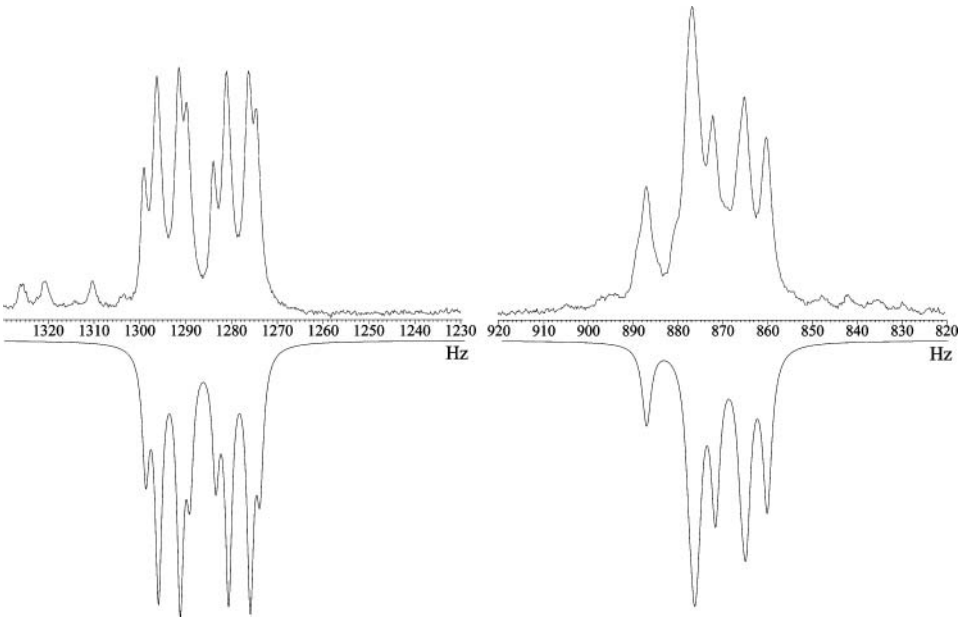


Figure 2 Experimental (top) and simulated (bottom) ^{1}H pattern for the α- and β-protons of **IIa–D** in CD_3OD; there are two three-spin systems (abbreviated MBX and MAX, where X is the P-atom: $^{2}J_{HD}$ is neglected) using a ratio of 2.0. For the major isomer: $^{3}J_{MB} = 4.9$, $^{2}J_{XM} = 15.2$, and $^{3}J_{XB} = 11.9$; H_M and H_B resonances at 1286.4 and 868.6 Hz, respectively. For the minor one: $^{3}J_{MA} = 9.3$, $^{2}J_{XM} = 15.0$, and $^{3}J_{XA} = 11.6$; H_M and H_A resonances at 1286.8 and 876.6 Hz, respectively. Spectral half-width = 2.3 Hz.

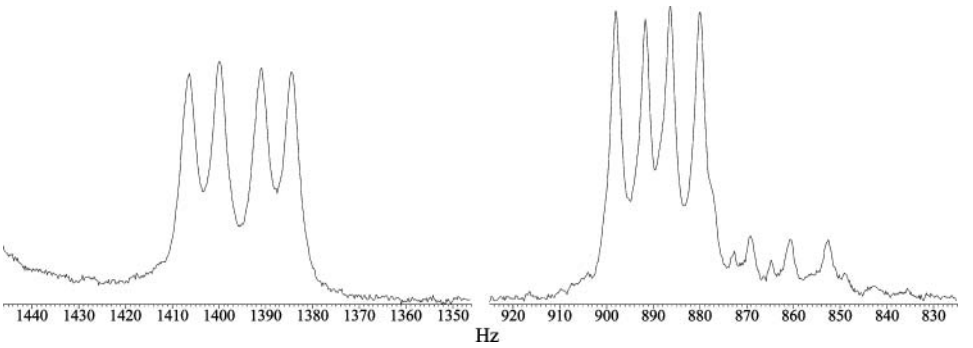


Figure 3 Experimental ^{1}H NMR pattern for the α- and β-protons of **IIb–D** in CD_3OD.

spectrum gave a d.r. of 7.5, while the ^{1}H pattern of the α- and β-protons of **IIi** (Figure 5) consists of two $MAXY_3$ spin systems. The major isomer is well simulated using $J_{MA} = 5.5$, $J_{MX} = 15.4$, $J_{AX} = 5.0$, $J_{AY} = 7.0$, $J_{YX} = 1.0$, $J_{MY} = 0$, and $\Delta_{MA} = 217.0$ Hz.

Thus, the α-Me group affects both the reactivity of the acid and the stereoselectivity of the product. The lower reactivity of **Ii** versus **Ia** likely results from the electron-donating Me group reducing the electrophilicity of the β-C atom. The higher d.r. for **IIi–D** (7.5 vs. ~2 for **IIa–D**) could be a result of the steric effect of the Me-group in an intermediate stage. Worth noting is that interaction of Ph_2PH with α-methylcinnamaldehyde affords $Ph_2PCH(Ph)CH(Me)CHO$ as a mixture of diastereomers with predominantly (*S,S*)- and (*R,R*)-chirality (d.r. ~20, after isolation).[10]

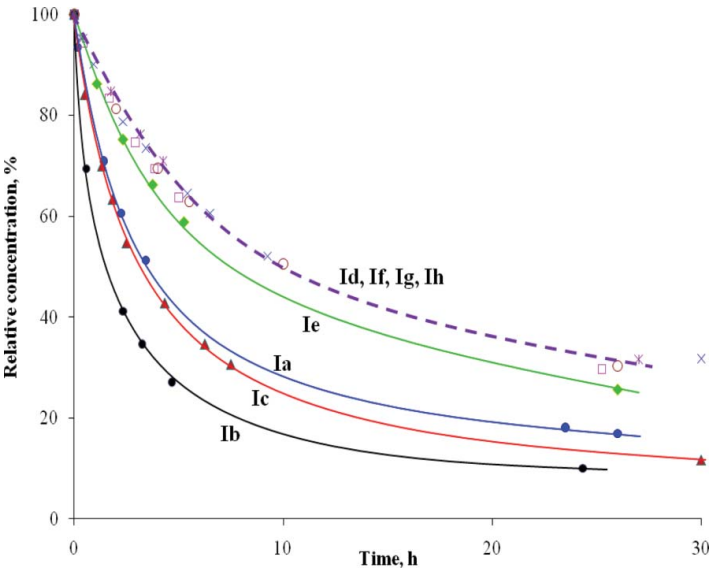


Figure 4 Relative concentration of cinnamic acids in the 1:1 reaction with THPP (r.t., Ar, CD_3OD) versus time; data determined from integrations of the α-proton signal of the acid and the β-proton signal of the phosphobetaine product. (Color figure available online).

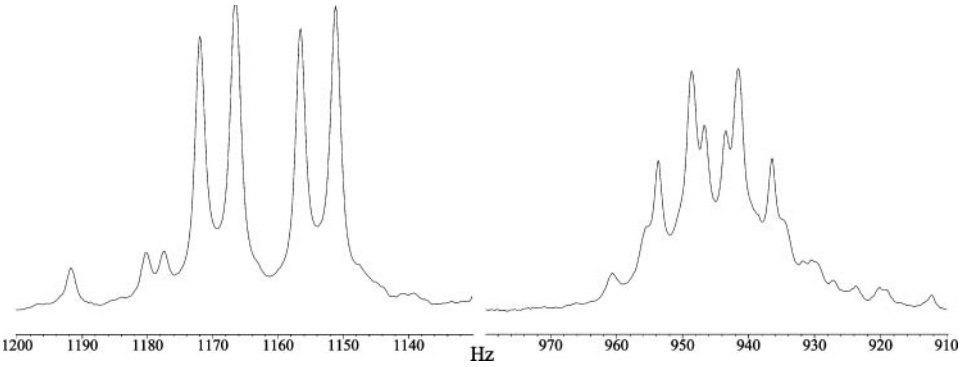


Figure 5 Experimental ^{1}H NMR pattern for the α- and β-protons of **IIi** in CD_3OD.

The β-methylcinnamic acid (**Ij**) reacts with THPP much more slowly than does **Ii**, only 40% of **IIj–D** ($\delta_P = 43.7$) being generated in CD_3OD at 60°C over 11 days (Scheme 4), presumably due to the steric effect of the Me at the β-position, where the phosphine attacks; **IIj–D** is formed as a diastereomeric mixture with d.r. ~2 (the same as for **IIa–D**), as estimated by integration within the $^1H\{^{31}P\}$ spectrum. Figure 6 shows the ^{1}H pattern for the α-protons of the non-deuterated product **IIj** in CD_3OD; in this three-spin ABX system (X is the P-atom), the diastereotopic α-protons are anisochronous by 14.2 Hz, the whole pattern being well simulated by using $J_{AB} = 15.5$, $J_{AX} = 8.5$, and $J_{BX} = 17.0$ Hz. In D_2O, the α-protons are anisochronous by 141.5 Hz and each proton is seen as a simple doublet of doublets with $J_{AB} = 15.2$, $J_{AX} = 11.0$, and $J_{BX} = 6.0$ Hz. Of note, the coupling constants of the α-protons to the P-atom in **IIj** are different, whereas in **IIa** they are equal ($J_{XA} = J_{XB} = 8.3$ Hz); this is likely due to more restricted rotation about the $\alpha-\beta$ bond in **IIj** caused by the steric effect of the β-Me. In the $^{31}P\{^1H\}$ spectrum of **IIj** in D_2O, the coproduct (**IVj**, see Scheme 2) is seen as a broad resonance at $\delta_P = \sim 14$, which is reasonable considering the chemical shift value of $[DO(CH_2)_3]_3PD^+$ in D_2O ($\delta_P = 17.0$,

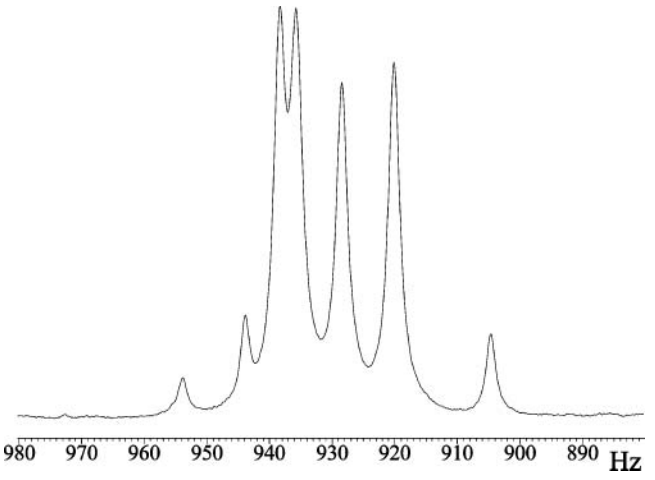
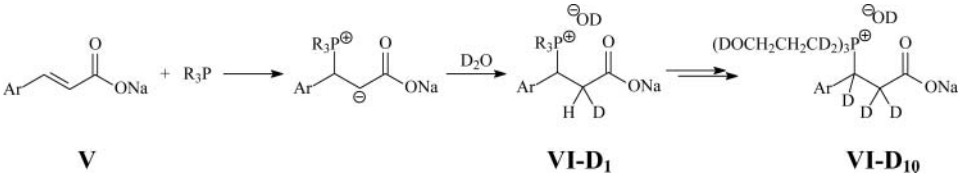


Figure 6 Experimental ^{1}H NMR pattern for the α-protons of **IIj** in CD_3OD.

t, $^1J_{PD} = 75$ Hz);[4,13] the corresponding $THPPH^+$/THPP equilibria in H_2O was discussed above.

The reaction of 3,4-$(MeO)_2$-cinnamic acid (**Ie**) with THPP in D_2O at r.t. under Ar for 24 h generated the monodeuterated salt **IIe-D** in 85% NMR-yield (d.r. ~1.3), with the remaining 15% being present as $THPPH^+$(cinnamate$^-$) (**IV-e**); in the corresponding reaction in CD_3OD, the d.r. was ~2. A parallel 1:1 reaction of the sodium salt of this acid (**V**) with THPP in D_2O occurs very slowly (Scheme 5) and, after 1 day, a low intensity $^{31}P\{^1H\}$ singlet at $\delta_P = 38.2$ was seen and attributed to the monodeuterated salt (**VI-D$_1$**). A $^{31}P\{^1H\}$ resonance of THPP seen at $\delta_P = -29.1$, and ^1H signals at $\delta_H = 1.43$, 1.60, and 3.58 for the associated γ-, δ-, and ε-protons, are close to those recorded for the neutral THPP, implying that **IVe** is not formed. Heating the reaction mixture to 60°C resulted in slow consumption of the THPP, with the α- and β-protons of **VI-D$_1$** now being detected as multiplets (cf. Figures 3 and 4) centered at $\delta_H = 2.90$ and 4.10, respectively; these are slightly upfield to those for the salt **IIe–D** ($\delta_H = 2.95$ and 4.16, respectively), reflecting somewhat higher electron density on these protons in **VI-D$_1$** vs. those in **IIe–D**. This must result from a balance between relative electrostatic effects of the two ionic $P^+ \ldots {}^-OD$ and $CO_2^- \ldots Na^+$ sites. The γ-protons of VI-D_1 are detected at $\delta_H = 2.24$ (see Scheme 1 for labeling of protons). In the course of the reaction, the α-, β- and γ-protons are exchanged with deuterons, and replacement of each of the β- and γ-proton results in an upfield-shift of the ^{31}P resonance of **VI** by ~0.1 ppm. After 5 days, the $^{31}P\{^1H\}$ resonance attributed to the deuterated product **VI-D$_{10}$** was detected at $\delta_P = 37.5$, and the ^1H spectrum of the mixture showed no resonances for the α-, β-, or γ-protons, while the δ- and ε-protons of VI-D_{10} were seen at $\delta_H = 1.67$ and 3.61. The presence of the Na^+ prevents formation of a zwitterionic structure, similar to that of **II**. In aqueous media, after the attack of THPP on the C=C bond of **V**, the phosphonium **VI-D$_1$** cation "acquires" the OD^- counterion which, as a strong base, leads to exchange of the β- and γ-protons adjacent to the P-atom via ylide intermediate species,[4,6a] and replacement of the acidic α-protons via acid–base interaction.



Scheme 5

CONCLUSIONS

As part of studies on the interaction of pulp constituents with tertiary phosphines, which is relevant in pulp bleaching, $[HO(CH_2)_3]_3P$ is shown to react with cinnamic acids (1:1) to form in moderate yield phosphonium zwitterions of a known type, in this case $[HO(CH_2)_3]_3P^+CH(Ar)CH_2CO_2^-$ (**II**). In acetone, the zwitterions precipitate with a minor product formed via neutralization of the ionic charges of **II** with the reactant acid and phosphine, but in aqueous solution this is slowly converted to **II**. The corresponding reactions in CD_3OD generate the diastereomers $[HO(CH_2)_3]_3P^+CH(Ar)CH(D)CO_2^-$ with

d.r. values that depend on substituent groups present in the organic acid. The reactivity of the cinnamic acids decreases in the order: 2-HO-cinnamic acid > 3-HO-cinnamic acid > cinnamic acid > 3,4-$(MeO)_2$-cinnamic acid > ferulic acid ≈ caffeic acid ≈ sinapic acid ≈ *p*-coumaric acid > α-methylcinnamic acid > β-methylcinnamic acid, all the naturally occurring acids having similar reactivity; a Me substituent at the C=C bond reduces the reactivity dramatically.

EXPERIMENTAL

General. All cinnamic acids were purchased from Aldrich and were used without purification. *Tris*(3-hydroxypropyl)phosphine (an oil, >80%)[4] was purchased from Strem and was also used without purification. The sodium salt of 3,4-dimethoxycinnamic acid was prepared by neutralization of the acid with NaOH. Regular distilled water and D_2O were saturated with Ar for 3 h under stirring. CD_3OD (Cambridge Isotope Laboratories) was used as received. Organic solvents were dried over the appropriate agents, distilled under N_2, degassed, and saturated with Ar. The NMR spectra were recorded on a Bruker AV300 spectrometer at 300 K (300 MHz for ^1H; 121 MHz for $^{31}P\{^1H\}$; 75 MHz for $^{13}C\{^1H\}$). A residual deuterated solvent proton (relative to external $SiMe_4$) and external 85% aq H_3PO_4 were used as references (br = broad, s = singlet, d = doublet, t = triplet, and m = multiplet; *J* values are given in Hertz). The ^1H spectra simulated by using the gNMR version 4 program, with *J* values to ± 0.3 Hz. Elemental analyses were performed using a Carlo Erba 1108 analyzer. Mass spectrometry was performed on a Bruker Esquire Electrospray (ESI) ion-trap instrument with samples dissolved in MeOH or H_2O, with positive ion polarity, scanning from 100−1000 m/z.

Preparation of $[HO(CH_2)_3]_3P^+CH(Ph)CH_2CO_2^-$ (IIa). A solution of THPP (70 mg, 0.34 mmol for 100% purity) and cinnamic acid (50 mg, 0.34 mmol) in O_2-free acetone (3 mL) was kept at r.t. for 24 h. The white product was filtered off, washed with acetone (∼1 mL), and dried in vacuo. Yield 82 mg (68%). Anal. Calcd. for $C_{18}H_{29}O_5P$ (356.39 g/mol): C 60.66, H 8.20. Found: C 60.3, H 8.1%. $^{31}P\{^1H\}$ NMR (D_2O), $\delta = 38.3$ s. ^1H NMR (D_2O), $\delta = 7.58-7.43$ (m, 5H, C_6H_5), 4.23 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.2, $^3J_{HH}$ 11.2, $^3J_{HH}$ 4.6 − see Figure 1), 3.67 (t, 6H, CH_2OH, $^3J_{HH}$ 6.0), 3.16−2.91 (m, 2H, CH_2CO_2 − see Figure 1), 2.34 (dt, 6H, PCH_2, $^2J_{PH}$ 12.7, $^3J_{HH}$ 8.5), 1.89−1.65 m (6H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (D_2O), $\delta = 177.6$ (d, *C*O_2, $^3J_{PC}$ 16), 133.3 (d, *ipso-C*, $^2J_{PC}$ 6), 131.0 (d, *m-C*, $^4J_{PC}$ 2), 130.6 (d, *p-C*, $^5J_{PC}$ 3), 130.3 (d, *o-C*, $^3J_{PC}$ 5), 62.4 (d, *C*H_2OH, $^3J_{PC}$ 17), 37.7 (d, P*C*H, $^1J_{PC}$ 44), 37.0 (s, *C*H_2CO_2), 25.1 (d, PCH_2CH_2, $^2J_{PC}$ 4), 15.7 (d, P*C*H_2, $^1J_{PC}$ 48). ESI-MS (MeOH): *m/z* 209.0 (5%) $[THPP + H]^+$, 357.1 (100%) $[M + H]^+$. According to NMR data (see text), the solid contains 17% of the byproduct **IIIa**.

$[HO(CH_2)_3]_3P^+CH(2\text{-}HOC_6H_4)CH_2CO_2^-$ (IIb). The procedure used follows that given for **IIa** except that 100 mg (0.48 mmol) of THPP and 78 mg (0.48 mmol) of 2-HO-cinnamic acid were used; 150 mg of a white solid (84%) were isolated. Anal. Calcd. for $C_{18}H_{29}O_6P$ (372.39 g/mol): C 58.06, H 7.85. Found: C 58.4, H 7.7%. $^{31}P\{^1H\}$ NMR (D_2O), $\delta = 39.3$ s. ^1H NMR (D_2O), $\delta = 7.38-7.27$ (m, 2H), 7.07−6.95 (m, 2H), 4.60 (br t, 1H, PC*H*), 3.60 (t, 6H, CH_2OH, $^3J_{HH}$ 6.0), 3.14−2.87 (m, 2H, CH_2CO_2), 2.32 (dt, 6H, PCH_2, $^2J_{PH}$ 12.9, $^3J_{HH}$ 8.2), 1.84−1.61 (m, 6H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (D_2O), $\delta = 177.9$ (d, *C*O_2, $^3J_{PC}$ 15), 155.9 (d, *o*-C-OH, $^3J_{PC}$ 5), 131.6 (d, *p-C*, $^5J_{PC}$ 2), 130.7 (br s), 122.6 (d, J_{PC} 1), 120.4 (d, *ipso-C*, $^2J_{PC}$ 5), 117.4 (d, J_{PC} 2), 62.5 (d, *C*H_2OH, $^3J_{PC}$ 17), 36.6 (s, *C*H_2CO_2), 31.2 (br s, P*C*H), 25.1 (d, PCH_2CH_2, $^2J_{PC}$ 4), 16.1 (d, P*C*H_2, $^1J_{PC}$ 48). ESI-MS (MeOH):

m/z 209.2 (10%) [THPP + H]$^+$, 373.3 (100%) [*M* + H]$^+$. The solid contains 15% of the byproduct **IIIb**.

[HO(CH$_2$)$_3$]$_3$P$^+$CH(3-HOC$_6$H$_4$)CH$_2$CO$_2^-$ (IIc). The procedure used follows that given for (**IIb**); 152 mg of a white solid (85%) was isolated. Anal. Calcd. for $C_{18}H_{29}O_6P$ (372.39 g/mol): C 58.06, H 7.85. Found: C 57.7, H 7.5%. $^{31}P\{^1H\}$ NMR (D_2O), $\delta = 38.3$ s. ^1H NMR (D_2O), $\delta = 7.30$ (t, 1H, $^3J_{HH}$ 7.8), 6.96−6.81 (m, 3H), 4.11 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.2, $^3J_{HH}$ 11.0, $^3J_{HH}$ 4.6), 3.59 (t, H, CH_2OH, $^3J_{HH}$ 6.0), 3.06−2.81 (m, 2H, CH_2CO$_2$), 2.25 (dt, 6H, PCH_2, $^2J_{PH}$ 12.5, $^3J_{HH}$ 8.3), 1.79−1.54 (m, 6H, PCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (D_2O), $\delta = 177.2$ (d, *C*O$_2$, $^3J_{PC}$ 16), 157.9 (d, *m*-C-OH, $^4J_{PC}$ 2), 134.9 (d, *ipso-C*, $^2J_{PC}$ 5), 132.4 (d, *m*-C, $^4J_{PC}$ 2), 122.2 (d, *o*-C, $^3J_{PC}$ 5), 117.5 (d, *p*-C, $^5J_{PC}$ 3), 117.1 (d, *o*-C, $^3J_{PC}$ 5), 62.3 (d, *C*H$_2$OH, $^3J_{PC}$ 17), 37.5 (d, P*C*H, $^1J_{PC}$ 44), 36.7 (s, *C*H$_2$CO$_2$), 25.1 (d, PCH$_2$*C*H$_2$, $^2J_{PC}$ 4), 15.7 (d, P*C*H$_2$, $^1J_{PC}$ 48). ESI-MS (MeOH): *m/z* 209.2 (9%) [THPP + H]$^+$, 373.3 (100%) [*M* + H]$^+$. The solid contains 12% of the byproduct **IIIc**.

[HO(CH$_2$)$_3$]$_3$P$^+$CH(4-HOC$_6$H$_4$)CH$_2$CO$_2^-$ (IId). The procedure used follows that given for (**IIb**); 147 mg of a white solid (83%) was isolated. Anal. Calcd. for $C_{18}H_{29}O_6P$ (372.39 g/mol): C 58.06, H 7.85. Found: C 58.4, H 7.5%. $^{31}P\{^1H\}$ NMR (D_2O), $\delta = 38.1$ s. ^1H NMR (D_2O), δ 7.30 (m, 2H), 6.96 (m, 2H), 4.14 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.3, $^3J_{HH}$ 11.0, $^3J_{HH}$ 4.6), 3.64 (t, 6H, CH_2OH, $^3J_{HH}$ 6.0), 3.07−2.84 (m, 2H, CH_2CO$_2$), 2.28 (dt, 6H, PCH_2, $^2J_{PH}$ 12.7, $^3J_{HH}$ 8.3), 1.85−1.61 (m, 6H, PCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (D_2O), $\delta =$ 177.3 (d, *C*O$_2$, $^3J_{PC}$ 16), 157.7 (d, *p*-C-OH, $^5J_{PC}$ 3), 131.7 (d, *o*-C, $^3J_{PC}$ 4), 124.4 (d, *ipso-C*, $^2J_{PC}$ 6), 117.7 (s, *m*-C), 62.3 (d, *C*H$_2$OH, $^3J_{PC}$ 17), 37.0 (s, *C*H$_2$CO$_2$), 36.9 (d, P*C*H, $^1J_{PC}$ 44), 25.1 (d, PCH$_2$*C*H$_2$, $^2J_{PC}$ 4), 15.7 (d, P*C*H$_2$, $^1J_{PC}$ 48). ESI-MS (MeOH): *m/z* 209.1 (52%) [THPP + H]$^+$, 373.3 (100%) [*M* + H]$^+$. The solid contains 17% of the byproduct **IIId**.

[HO(CH$_2$)$_3$]$_3$P$^+$CH[3,4-(MeO)$_2$C$_6$H$_3$]CH$_2$CO$_2^-$ (IIe). The procedure used follows that given for (**IIb**) except that 100 mg (0.48 mmol) of 3,4-(MeO)$_2$-cinnamic acid was used; 135 mg of a white solid (68%) was isolated. Anal. Calcd. for $C_{20}H_{33}O_7P$ (416.44 g/mol): C 57.68, H 7.99. Found: C 57.3, H 8.4%. $^{31}P\{^1H\}$ NMR (D_2O), $\delta = 38.1$ s. ^1H NMR (D_2O), δ = 7.09−6.96 (m, 3H, C$_6H_3$), 4.16 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.0, $^3J_{HH}$ 10.8, $^3J_{HH}$ 4.6), 3.88 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.62 (t, 6H, CH_2OH, $^3J_{HH}$ 6.0), 3.09−2.83 (m, 2H, CH_2CO$_2$), 2.29 (dt, 6H, PCH_2, $^2J_{PH}$ 12.3, $^3J_{HH}$ 8.3), 1.82−1.59 (m, 6H, PCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (D_2O), $\delta = 177.5$ (d, *C*O$_2$, $^3J_{PC}$ 16), 150.1 (d, *p-C*-OMe and *m-C*-OMe, $^3J_{PC}$ 2), 125.8 (d, *ipso-C*, $^2J_{PC}$ 6), 123.2 (d, *o*-C, $^3J_{PC}$ 5), 113.8 (d, *m*-C, $^4J_{PC}$ 2), 113.6 (d, *o*-C, $^3J_{PC}$ 5), 62.3 (d, *C*H$_2$OH, $^3J_{PC}$ 17), 57.2 (s, O*C*H$_3$), 57.1 (s, O*C*H$_3$), 37.4 (d, P*C*H, $^1J_{PC}$ 43), 37.1 (s, *C*H$_2$CO$_2$), 25.1 (d, PCH$_2$*C*H$_2$, $^2J_{PC}$ 4), 15.7 (d, P*C*H$_2$, $^1J_{PC}$ 48). ESI-MS (MeOH): *m/z* 209.2 (100%) [THPP + H]$^+$, 417.4 (95%) [*M* + H]$^+$. The solid contains 20% of the byproduct **IIIe**.

[HO(CH$_2$)$_3$]$_3$P$^+$CH(4-HO-3-MeO-C$_6$H$_3$)CH$_2$CO$_2^-$ (IIf). The procedure used follows that given for **IIb** except that 93 mg (0.48 mmol) of ferulic acid was used; 90 mg of a white solid (47%) was isolated. Anal. Calcd. for $C_{19}H_{31}O_7P$ (402.42 g/mol): C 56.71, H 7.76. Found: C 56.4, H 7.9%. $^{31}P\{^1H\}$ NMR (D_2O), $\delta = 38.0$ s. ^1H NMR (D_2O), $\delta =$ 7.04−6.88 (m, 3H, C$_6H_3$), 4.14 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.4, $^3J_{HH}$ 11.0, $^3J_{HH}$ 4.8), 3.91 (s, 3H, CH_3O), 3.65 (t, 6H, CH_2OH, $^3J_{HH}$ 5.9), 3.09−2.84 (m, 2H, CH_2CO$_2$), 2.32 (dt, 6H, PCH_2, $^2J_{PH}$ 12.3, $^3J_{HH}$ 8.3), 1.84−1.61 (m, 6H, PCH$_2$CH_2). $^{13}C\{^1H\}$ NMR (D_2O), $\delta =$ 177.5 (d, *C*O$_2$, $^3J_{PC}$ 16), 149.4 (d, *p*-C, $^5J_{PC}$ 2), 147.0 (d, *m-C*-OMe, $^4J_{PC}$ 3), 125.2 (d, *ipso-C*, $^2J_{PC}$ 6), 123.3 (d, *o*-C, $^3J_{PC}$ 5), 117.6 (d, *m*-C, $^4J_{PC}$ 2), 114.3 (d, *o*-C, $^3J_{PC}$ 4), 62.4 (d, *C*H$_2$OH, $^3J_{PC}$ 17), 57.4 (s, O*C*H$_3$), 37.3 (d, P*C*H, $^1J_{PC}$ 45), 37.0 (s, *C*H$_2$CO$_2$), 25.1

(d, PCH_2CH_2, $^2J_{PC}$ 5), 15.7 (d, PCH_2, $^1J_{PC}$ 48). ESI-MS (MeOH-H_2O): *m/z* 209.2 (20%) [THPP + H]$^+$, 403.3 (100%) [*M* + H]$^+$. The solid contains 20% of the byproduct **IIIf**.

$[HO(CH_2)_3]_3P^+CH[3,4\text{-}(HO)_2C_6H_3]CH_2CO_2^-$ (IIg). The procedure used follows that given for **IIb** except that 87 mg (0.48 mmol) of caffeic acid was used; 112 mg of a yellowish solid (60%) was isolated. Anal. Calcd. for $C_{18}H_{29}O_7P$ (388.39 g/mol): C 55.66, H 7.53. Found: C 54.9, H 8.0%. $^{31}P\{^1H\}$ NMR (D_2O), δ = 38.0 s. ^1H NMR (D_2O), δ = 7.01−6.81 (m, 3H, C_6H_3), 4.06 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.0, $^3J_{HH}$ 10.8, $^3J_{HH}$ 4.8), 3.64 (t, 6H, CH_2OH, $^3J_{HH}$ 6.0), 3.03−2.81 (m, 2H, CH_2CO_2), 2.29 (dt, 6H, PCH_2, $^2J_{PH}$ 12.7, $^3J_{HH}$ 8.5), 1.85−1.60 (m, 6H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (D_2O), δ = 177.6 (d, CO_2, $^3J_{PC}$ 16), 146.2 (overlapping *p-C*-OH and *m-C*-OH), 125.1 (d, *ipso-C*, $^2J_{PC}$ 6), 122.7 (d, *o*-C, $^3J_{PC}$ 5), 118.2 (s, *m*-C), 117.7 (d, *o*-C, $^3J_{PC}$ 4), 62.3 (d, CH_2OH, $^3J_{PC}$ 16), 37.0 (d, PCH, $^1J_{PC}$ 44), 36.9 (s, CH_2CO_2), 25.1 (d, PCH_2CH_2, $^2J_{PC}$ 4), 15.7 (d, PCH_2, $^1J_{PC}$ 48). ESI-MS (H_2O): *m/z* 209.2 (17%) [THPP + H]$^+$, 389.2 (100%) [*M* + H]$^+$. The solid contains 20% of the byproduct **IIIg**.

$[HO(CH_2)_3]_3P^+CH[4\text{-}HO\text{-}3,5\text{-}(MeO)_2C_6H_2]CH_2CO_2^-$ (IIh). The procedure used follows that given for **IIb** except that 107 mg (0.48 mmol) of sinapic acid was used; 118 mg of a yellowish solid (57%) was isolated. Anal. Calcd. for $C_{20}H_{33}O_8P$ (432.44 g/mol): C 55.55, H 7.69. Found: C 55.4, H 7.3%. $^{31}P\{^1H\}$ NMR (D_2O), δ = 38.1 s. ^1H NMR (D_2O), δ = 6.72 (d, 2H, C_6H_2, $^4J_{PH}$ 2.3), 4.14 (ddd, 1H, PC*H*, $^2J_{PH}$ 15.2, $^3J_{HH}$ 11.2, $^3J_{HH}$ 4.6), 3.90 (s, 6H, CH_3O), 3.65 (t, 6H, CH_2OH, $^3J_{HH}$ 6.0), 3.10−2.86 (m, 2H, CH_2CO_2), 2.19 (dt, 6H, PCH_2, $^2J_{PH}$ 12.3, $^3J_{HH}$ 8.5), 1.70−1.45 (m, 6H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (D_2O), δ = 177.5 (d, CO_2, $^3J_{PC}$ 16), 149.7 (d, *m*-C, $^4J_{PC}$ 3), 136.1 (d, *p*-C, $^5J_{PC}$ 3), 124.6 (d, *ipso-C*, $^2J_{PC}$ 6), 107.9 (s, *o*-C), 62.4 (d, CH_2OH, $^3J_{PC}$ 16), 57.9 (s, OCH_3), 37.8 (d, PCH, $^1J_{PC}$ 44), 36.8 (s, CH_2CO_2), 25.1 (d, PCH_2CH_2, $^2J_{PC}$ 5), 15.8 (d, PCH_2, $^1J_{PC}$ 48). ESI-MS (MeOH): *m/z* 209.2 (70%) [THPP + H]$^+$, 433.4 (100%) [*M* + H]$^+$. The solid contains the byproduct **IIIh** (20%).

$[HO(CH_2)_3]_3P^+CH(Ph)CH(Me)CO_2^-$ (IIi). The procedure used follows that given for **IIb** except that 79 mg (0.48 mmol) of α-methylcinnamic acid was used and the reaction mixture was heated at 60°C for 2 days; ∼90 mg of a white, viscous solid (∼50%) was isolated. $^{31}P\{^1H\}$ NMR (D_2O), δ = 37.4 s (major diastereomer), δ = 37.9 s (minor): d.r. = 10. ^1H NMR (D_2O), δ = 7.55−7.29 (m, 5H, C_6H_5), 3.89 (dd, 1H, PC*H*, $^3J_{HH}$ 8.9, $^2J_{PH}$ 14.5), 3.60 (t, 6H, CH_2OH, $^3J_{HH}$ 5.8), 3.24 (m, 1H, C*H*Me), 2.45−2.25 (m, 6H, PCH_2), 1.78−1.58 (m, 6H, PCH_2CH_2), 1.27 (d, 3H, $CHCH_3$, $^3J_{HH}$ 6.9). $^{13}C\{^1H\}$ NMR (D_2O), δ = 180.3 (d, CO_2, $^3J_{PC}$ 10), 132.0 (d, *ipso*-C, $^2J_{PC}$ 5), 129.9 (d, *o-C*, $^3J_{PC}$ 4), 129.6 (d, *m-C*, $^4J_{PC}$ 2), 129.2 (d, *p-C*, $^5J_{PC}$ 3), 61.1 (d, CH_2OH, $^3J_{PC}$ 17), 43.5 (s, CH_2CO_2), 43.1 (d, PCH, $^1J_{PC}$ 43), 24.1 (d, PCH_2CH_2, $^2J_{PC}$ 5), 16.8 (d, CH_3, $^3J_{PC}$ 5), 16.4 (d, PCH_2, $^1J_{PC}$ 48). ESI-MS (MeOH): *m/z* 371.1 [*M* + H]$^+$; M_{calcd} 370.2. The solid contains 25% of the byproduct **IIIi**.

Reaction of THPP and β-methylcinnamic acid in methanol. This reaction was performed according to the procedure described above except for that the reaction mixture was heated at 60°C for 11 days in MeOH. After removal of MeOH, a white residue was washed three times with acetone and dried overnight in vacuo. The resulting viscous-like solid was dissolved in D_2O. $[HO(CH_2)_3]_3P^+C(Me)(Ph)CH_2CO_2^-$ (**IIj**): $^{31}P\{^1H\}$ NMR (D_2O), δ = 43.5 s. ^1H NMR (D_2O), δ = 7.60−7.35 (m, 5H, C_6H_5), 3.58 (t, 6H, CH_2OH, $^3J_{HH}$ 6), 3.35 (dd, 1H, CH_AH_B, $^2J_{HH}$ 15.2, $^3J_{PH}$ 11.0), 2.87 (dd, 1H, CH_AH_B, $^2J_{HH}$ 15.2, $^3J_{PH}$ 6.0), 2.35−2.17 (m, 6H, PCH_2), 2.02 (d, 3H, CH_3, $^2J_{PH}$ 18), 1.72−1.43 (m, 6H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (D_2O), δ = 175.4 (d, CO_2, $^3J_{PC}$ 17), 136.2 (d, *ipso-C*, $^2J_{PC}$ 5),

129.5 (d, *m-C*, $^4J_{PC}$ 3), 128.4 (s, *p-C*), 127.5 (d, *o-C*, $^3J_{PC}$ 5), 61.1 (d, *C*H_2OH, $^3J_{PC}$ 16), 42.1 (s, (*C*H_2CO_2), 40.8 (d, P*C*H, $^1J_{PC}$ 39), 24.4 (d, PCH_2*C*H_2, $^2J_{PC}$ 5), 17.1 (s, *C*H_3), 14.1 (d, P*C*H_2, $^1J_{PC}$ 46).

NMR investigation of the 1:1 reaction of THPP with cinnamic acids in CD_3OD. In a glove-box, THPP (24.0 mg, 0.115 mmol) and an acid (0.115 mmol; cinnamic acid 17.0 mg, 2-, 3-, 4-HO-cinnamic acid 18.9 mg, 3,4-$(MeO)_2$-cinnamic acid 24.0 mg, ferulic acid 22.3 mg, caffeic acid 20.7 mg, sinapic acid 25.8 mg, α-, β-methylcinnamic acid 18.6 mg) were dissolved in CD_3OD (1 g, 1.12 mL). The mixture was stirred for 5 min at r.t., when 0.7 mL of the solution was transferred into a J-Young NMR tube under Ar; the NMR spectra were then recorded periodically.

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