Inorg. Chem. **2007**, *46*, 9389–9399

Interaction of Tertiary Phosphines with Lignin-Type, α,β-Unsaturated Aldehydes in Water

Dmitry V. Moiseev,[†] Brian O. Patrick,[†] Brian R. James,*[,†] and Thomas Q. Hu[‡]

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1, and Pulp and Paper Research Institute of Canada, Vancouver, British Columbia, Canada V6S 2L9

Received April 19, 2007

To learn more about the bleaching action of pulps by (hydroxymethyl)phosphines, lignin chromophores, such as the α,β-unsaturated aromatic aldehydes, sinapaldehyde, coniferylaldehyde, and coumaraldehyde, were reacted with the tertiary phosphines $R_2R'P$ [R = R′ = Me, Et, $(CH_2)_3OH$, ^{i}Pr, *cyclo*-C_6H_{11}, $(CH_2)_2CN$; R = Me or Et, R′ = Ph; R = Ph, R′ = Me, *m*-$NaSO_3$-C_6H_4] in water at room temperature under argon. In all cases, initial nucleophilic attack of the phosphine occurs at the activated C═C bond to form a zwitterionic monophosphonium species. With the phosphines PR_3 [R = Me, Et, $(CH_2)_3OH$] and with $R_2R'P$ (R = Me or Et, R′ = Ph), the zwitterion undergoes self-condensation to give a bisphosphonium zwitterion that can react with aqueous HCl to form the corresponding dichloride salts (as a mixture of *R,R*- and *S,S*-enantiomers); X-ray structures are presented for the bisphosphonium chlorides synthesized from the Et_3P and Me_3P reactions with sinapaldehyde. With the more bulky phosphines, $^i Pr_3P$, $MePPh_2$, (*cyclo*-$C_6H_{11})_3P$, and $Na[Ph_2P(m\text{-}SO_3\text{-}C_6H_4)]$, only an equilibrium of the monophosphonium zwitterion with the reactant aldehyde is observed. The weakly nucleophilic $[NC(CH_2)_2]_3P$ does not react with sinapaldehyde. An analysis of some exceptional ^{1}H NMR data within the prochiral phosphorus centers of the bisphosphonium chlorides is also presented.

Introduction

Investigations by our group have revealed that water-soluble phosphines, particularly, tris(hydroxymethyl)phosphine, $(HOCH_2)_3P$, are excellent bleaching agents for pulps.[1] α,β-Unsaturated aromatic aldehydes are considered to be one of the major chromophores responsible for the color of lignin and mechanical pulps.[2] We reported recently[3] that cinnamaldehyde reacts with tris(3-hydroxypropyl)phosphine, $[HO(CH_2)_3]_3P$, used as a model bleaching agent, to give two isomeric products, 2-benzyl-5-phenyl-pent-2,4-dienal and 5-phenyl-2-(phenylmethylene)-4-pentenal, via formation of unstable phosphonium salts. This earlier publication[3] presented a summary of the literature on reactions between phosphines and α,β-unsaturated carbonyl-containing compounds (specifically acids, ketones, esters, and quinones) and was, to the best of our knowledge, the first to report on interaction of phosphines with α,β-unsaturated aromatic aldehydes in aqueous media, although a patent had suggested a reaction based on measured differences in phosphine concentrations in systems in the absence and presence of crotonaldehyde.[4]

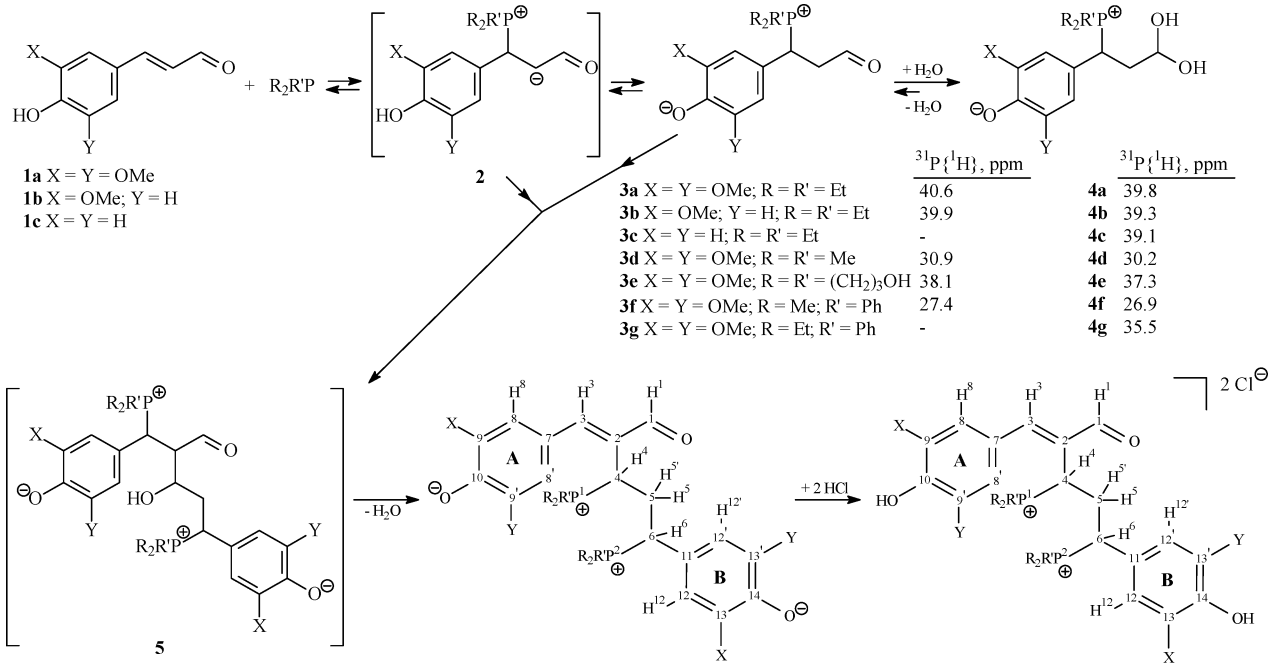
This current paper describes the interaction in aqueous media of tertiary phosphines with some aldehyde moieties found in lignin, namely, sinapaldehyde (**1a**), coniferylaldehyde (**1b**), and coumaraldehyde (**1c**), which are substituted cinnamaldehydes (see Scheme 1). These aldehydes possess an OH group in the position *para* to the unsaturated aliphatic chain, and reactivity different from that of cinnamaldehyde

* To whom correspondence should be addressed. E-mail: brj@chem.ubc.ca. Phone: 604-822-2847.
† University of British Columbia.
‡ Pulp and Paper Research Institute of Canada.

(1) (a) Hu, T. Q.; James, B. R.; Yawalata, D.; Ezhova, M. B. *J. Pulp Pap. Sci.* **2004**, *30*, 233. (b) Hu, T. Q.; James, B. R.; Yawalata, D.; Ezhova, M. B. World Patent PCT WO 2004 070110 A1, Aug 2004. (c) Hu, T. Q.; James, B. R.; Yawalata, D.; Ezhova, M. B.; Chandra, R. *J. Pulp Pap. Sci.* **2005**, *31*, 69. (d) Hu, T. Q.; James, B. R.; Yawalata, D.; Ezhova, M. B. *J. Pulp Pap. Sci.* **2006**, *32*, 131. (e) Chandra, R.; Hu, T. Q.; James, B. R.; Ezhova, M. B. *J. Pulp Pap. Sci.* **2007**, *33*, 15.
(2) (a) Adler, E. *Paperi ja Puu* **1961**, *11*, 634. (b) Pew, J. C.; Connors, W. J. *Tappi J.* **1971**, *54*, 245.
(3) Moiseev, D. V.; James, B. R.; Hu, T. Q. *Inorg. Chem.* **2007**, *46*, 4704.
(4) (a) Bryant, D. R.; Galley, R. A. (Union Carbide Corporation) U.S. Patent 4,283,304, Aug 1981. (b) Bryant, D. R. In *Catalyst Separation, Recovery and Recycling*; Cole-Hamilton, D., Tooze, R., Eds.; Springer: Dordrecht, The Netherlands, 2006; Chapter 2.

10.1021/ic7007478 CCC: $37.00
Published on Web 10/03/2007

Scheme 1



	$^{31}P\{^1H\}$, ppm
3a X = Y = OMe; R = R' = Et	40.6
3b X = OMe; Y = H; R = R' = Et	39.9
3c X = Y = H; R = R' = Et	-
3d X = Y = OMe; R = R' = Me	30.9
3e X = Y = OMe; R = R' = $(CH_2)_3OH$	38.1
3f X = Y = OMe; R = Me; R' = Ph	27.4
3g X = Y = OMe; R = Et; R' = Ph	-

	$^{31}P\{^1H\}$, ppm
4a	39.8
4b	39.3
4c	39.1
4d	30.2
4e	37.3
4f	26.9
4g	35.5

	$^{31}P\{^1H\}$, ppm
6a	43.1 (P^1); 40.6 (P^2)
6b	44.6 (P^1); 41.8 (P^2)
6c	43.0 (P^1); 39.5 (P^2)
6d	31.9 (P^1); 30.8 (P^2)
6e	40.4 (P^1); 38.1 (P^2)
6f	29.4 (P^1); 27.4 (P^2)
6g	37.4 (P^1); 36.2 (P^2)

	$^{31}P\{^1H\}$, ppm
7a	45.0 (P^1); 42.5 (P^2)
7b	see text
7c	45.0 (P^1); 42.3 (P^2)
7d	32.7 (P^1); 31.6 (P^2)
7e	40.8 (P^1); 38.3 (P^2)
7f	30.1 (P^1); 28.7 (P^2)
7g	37.9 (P^1); 37.0 (P^2)

was anticipated on the basis of our earlier work on differences in reaction of $[HO(CH_2)_3]_3P$ with a range of substituted benzaldehydes;[5] indeed, a new type of "dimeric" diphosphonium salt has been realized with these *p*-OH-substituted cinnamaldehyde systems.

Experimental Section

General. 3,5-Dimethoxy-4-hydroxycinnamaldehyde (sinapaldehyde, **1a**) and 4-hydroxy-3-methoxycinamaldehyde (coniferylaldehyde, **1b**) were used as received from Aldrich, while 4-hydroxycinnamaldehyde (coumaraldehyde, **1c**) was prepared according to the literature.[6] Tris(3-hydroxypropyl)phosphine (an oil, >80%), Et_3P, Me_2PPh, $MePPh_2$ $^iPr_3P$ (Strem products), and Me_3P (1.0 M solution in toluene) and Et_2PPh (Aldrich products) were used without purification; $(NCCH_2CH_2)_3P$,[7] $Na[Ph_2P(m\text{-}SO_3\text{-}C_6H_4)]$[8] were prepared according to literature methods. Regular distilled water and D_2O were saturated with Ar for 3 h under stirring. Organic solvents were dried over the appropriate agents and distilled under N_2. ^{31}P NMR spectra were recorded on a Bruker AV300 instrument, and ^1H, ^2D, and $^{13}C\{^1H\}$ NMR spectra were recorded on an AV400 spectrometer (unless stated otherwise); all NMR spectra were measured in D_2O at 300 K (unless stated otherwise). 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). When necessary, assignments were made by use of $^1H-^1H$, $^1H-^{13}C\{^1H\}$ (HSQC and HMBC), $^1H-^{31}P\{^1H\}$, and $^{31}P\{^1H\}-^{31}P\{^1H\}$ NMR correlation spectroscopies. UV−vis spectra were recorded in H_2O on an HP 8452A Diode-Array spectrometer at room temperature (RT, ~20 °C) with a quartz cell (1 cm). Elemental analyses were performed on Carlo Erba 1108 analyzer. Mass spectrometry was generally performed on a Bruker Esquire electrospray (ESI) ion-trap spectrometer with samples dissolved in water, with positive ion polarity scanning from 60 to 1000 *m/z*; a Bruker Biflex MALDI-TOF spectrometer was also used.

Preparation of the Bis(zwitterionic) Compound 6a. Et_3P (60 mg, 0.51 mmol) was added to a suspension of **1a** (100 mg, 0.48 mmol) in water (5 mL) under Ar. The reaction mixture was stirred for 3 days at RT (or 3 h at 50 °C) and monitored periodically by $^{31}P\{^1H\}$ NMR. After removal of water from the resulting dark red solution, a blackish "electrostatic" residue of **6a** was obtained. Yields of **6a** (and **6b**−**g**, see below) were high but were difficult to quantify because of the nature of the materials; no P-containing compounds, other than small amounts (~5%) of phosphine oxides, were seen in the $^{31}P\{^1H\}$ spectra. $^{31}P\{^1H\}$ NMR: δ 43.1 (d, $^4J_{PP}$ = 3, P^1), 40.6 (d, $^4J_{PP}$ = 3, P^2). ^1H NMR: δ 9.30 (s, 1H, H^1), 7.67 (s, 1H, H^3), 6.61 (s, 1H, H^{12}), 6.45 (s, 2H, $H^{8,8'}$), 6.09 (s, 1H, $H^{12'}$), 3.98 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx 13$, 1H, H^4 ($^1H\{^{31}P\}$: d, $^3J_{HH}$ = 11)], 3.80 (s, 3H, OCH_3^{13}), 3.53 (s, 6H, $OCH_3^{9,9'}$), 3.36 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx 14$, 1H, H^6 ($^1H\{^{31}P\}$: d, $^3J_{HH}$ = 13)], 3.19 (br m, 1H, H^5, overlapping with $OCH_3^{13'}$), 3.17 (s, 3H, $OCH_3^{13'}$), 2.48 (br m, 1H, $H^{5'}$), 2.36−2.01 (m, 12H, PCH_2), 1.22−0.91 (m, 18H, PCH_2CH_3). $^{13}C\{^1H\}$ NMR: δ 197.0 (s, C^1), 162.9 (d, $^3J_{PC}$ = 6.1, C^3), 158.8 (s, C^{10}), 150.8 (s, $C^{9,9'}$), 150.7 (d, $^4J_{PC}$ = 2.3, C^{13}), 150.6

(5) Moiseev, D. V.; James, B. R.; Hu, T. Q. *Inorg. Chem.* **2006**, *45*, 10338.
(6) Daubresse, N.; Francesch, C.; Mhamdi, F.; Rolando, C. *Synthesis* **1994**, 369.
(7) Vullo, W. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 346.
(8) Joó, F.; Kovacs, J.; Katho, A.; Benyei, A. C.; Darensbourg, D. J. *Inorg. Synth.* **1998**, *32*, 1.

(d, $^4J_{PC}$ = 2.3, $C^{13'}$), 144.5 (s, C^{14}), 118.5 (d, $^2J_{PC}$ = 6.1, C^2), 114.6 (s, C^7), 113.5 (d, $^2J_{PC}$ = 5.4, C^{11}), 111.9 (br s, $C^{8,8'}$), 111.1 (d, $^3J_{PC}$ = 6.1, $C^{12'}$), 104.3 (d, $^3J_{PC}$ = 3.1, C^{12}), 56.8 (s, OCH_3^{13}), 55.9 (s, $OCH_3^{9,9'}$), 55.5 (s, $OCH_3^{13'}$), 36.7 (dd, $^1J_{PC}$ = 45.1, $^3J_{PC}$ = 13.0, C^6), 28.8 (dd, $^1J_{PC}$ = 45.9, $^3J_{PC}$ = 13.8, C^4), 24.6 (s, C^5), 12.0 (d, $^1J_{PC}$ = 45.9, $P^1CH_2CH_3$), 10.7 (d, $^1J_{PC}$ = 46.7, $P^2CH_2CH_3$), 5.5 (d, $^2J_{PC}$ = 6.1, $P^1CH_2CH_3$), 4.9 (d, $^2J_{PC}$ = 5.4, $P^2CH_2CH_3$). UV−vis: 270, 450 nm ($\epsilon_{450} \approx 4 \times 10^4$ mol^{-1} cm^{-1}). Low-resolution ESI MS (H_2O): the dication of the protonated form of **6a** [*m*/2*z* 318.3 (100%, [**6a** + 2H]$^{2+}$), calcd 318.7], and the cation of the protonated form of the monophosphonium salt [*m*/*z* 517.4 (65%, [**6a** − Et_3P + H]$^+$), calcd 517.2] were detected.

Bis(zwitterionic) Compound 6b (Mixture of α- and *β*-Atropisomers). This almost-black solid was prepared by the procedure given for **6a** except that 200 mg (1.12 mmol) of coniferylaldehyde and 140 mg (1.19 mmol) of Et_3P were used. Spectroscopic data for the bis(zwitterionic) compounds **6b** (mixture of α- and *β*-atropisomers) and **6c**−**g** are given in the Supporting Information (Table S1).

Compound 6c. The compound was prepared by the procedure given for **6a** except that 90 mg (0.61 mmol) of coumaraldehyde and 76 mg (0.64 mmol) of Et_3P were used (see Table S1).

Compound 6d. The compound was prepared by the procedure given for **6a** except that Me_3P was added as 1.0 M solution in toluene (500 *μ*L, 0.5 mmol), and the mixture was stirred for 5 days at RT. Removal of water gave a blackish residue of **6d** (see Table S1).

Compound 6e. The procedure used was as described given for **6a** except that 100 mg of $[HO(CH_2)_3]_3P$ (0.48 mmol, assuming 100% purity) was used (see Table S1).

Compound 6f. The procedure given for **6a** (but with Me_2PPh) was used, although the reaction mixture was stirred for 8 h at RT.; a blackish residue of **6f** was obtained after removal of the water (see Table S1).

Compound 6g. The procedure given for **6a** (but with Et_2PPh) was used (see Table S1).

Preparation of the Bis(phosphonium) Dichloride 7a. The compound was prepared by addition of HCl (0.18 mL, 10% aq solution) to the dark red solution containing **6a**, obtained as described above. The mixture turns yellow, and after removal of water, the resulting yellow residue was dried under vacuum overnight and recrystallized from $CHCl_3$. Yield: ∼100 mg, 60%. Anal. Calcd for $C_{34}H_{54}Cl_2O_7P_2$: C, 57.71; H, 7.69. Found: C, 57.35; H, 7.84. $^{31}P\{^1H\}$ NMR: *δ* 45.0 (s, P^1), 42.5 (s, P^2). ^1H NMR: *δ* 9.63 (s, 1H, H^1), 7.96 (s, 1H, H^3), 6.70 (s, 1H, H^{12}), 6.47 (s, 2H, $H^{8,8'}$), 6.21 (s, 1H, $H^{12'}$), 3.98 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx$ 13, 1H, H^4 ($^1H\{^{31}P\}$: d,$^3J_{HH}$ = 11)], 3.92 (s, 3H, CH_3O^{13}), 3.72 (s, 6H, CH_3O^9), 3.52 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx$ 14, 1H, H^6 ($^1H\{^{31}P\}$: d, $^3J_{HH}$ = 13)], 3.41 (s, 3H, $CH_3O^{13'}$), 3.12 (br m, 1H, H^5), 2.70 (br m, 1H, $H^{5'}$), 2.58−2.34 (m, 6H, $P^1CH_2CH_3$), 2.27 (dq, $^2J_{PH}$ = 12.6, $^3J_{HH}$ = 7.6, 6H, $P^2CH_2CH_3$), 1.29 (dt, $^3J_{PH}$ = 18.5, $^3J_{HH}$ = 7.5, 9H, $P^1CH_2CH_3$), 1.09 (dt, $^3J_{PH}$ = 18.0, $^3J_{HH}$ = 7.7, 9H, $P^2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (75 Hz): *δ* 199.0 (s, C^1), 162.1 (d, $^3J_{PC}$ = 7.5, C^3), 148.7 (d, $^4J_{PC}$ = 2.9, C^{13}), 148.3 (d, $^4J_{PC}$ = 2.3, $C^{13'}$), 147.6 (s, C^9), 139.5 (s, C^{10}), 135.3 (d, $^5J_{PC}$ = 3.4, C^{14}), 126.5 (d, $^2J_{PC}$ = 5.7, C^2), 123.8 (d, $^4J_{PC}$ = 1.1, C^7), 119.8 (d, $^2J_{PC}$ = 5.7, C^{11}), 109.6 (d, $^3J_{PC}$ = 5.7, $C^{12'}$), 108.8 (s, $C^{8,8'}$), 102.8 (d, $^3J_{PC}$ = 2.3, C^{12}), 56 (s, CH_3O^{13}), 56.2 (s, CH_3O^9), 55.6 (s, $CH_3O^{13'}$), 36.4 (dd, $^1J_{PC}$ = 44.5, $^3J_{PC}$ = 12.9, C^6), 28.6 (dd, $^1J_{PC}$ = 46.0, $^3J_{PC}$ = 13.8, C^4), 24.4 (s, C^5), 12.3 (d, $^1J_{PC}$ = 46.0, P^1CH_2), 10.7 (d, $^1J_{PC}$ = 46.6, P^2CH_2), 5.8 (d, $^2J_{PC}$ = 5.7, $P^1CH_2CH_3$), 5.1 (d, $^2J_{PC}$ = 5.7, $P^2CH_2CH_3$). UV−vis: 250, 368 nm (ϵ_{368} = 18,800 mol^{-1} cm^{-1}).

Table 1. Crystallographic Data for **7a** and **7d**

	7a	**7d**
empirical formula	$C_{40}H_{70}O_9P_2Cl_2$	$C_{30}H_{50}O_9P_2Cl_2$
fw	827.80	687.54
cryst color, habit	pale yellow, prism	yellow, prism
cryst size, mm^3	0.30 × 0.15 × 0.07	0.25 × 0.25 × 0.35
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No.14)
a, Å	10.810(2)	10.186(1)
b, Å	14.866(2)	31.887(3)
c, Å	15.253(3)	11.314(1)
V, Å^3	2306.1(7)	3593.4(6)
Z	2	4
ρ_{calcd}, g/cm^3	1.192	1.271
F(000)	892.00	1464.00
μ, cm^{-1}	2.58	3.17
total reflns	16023	25943
unique reflns	5964	6455
R_{int}	0.073	0.047
variables	507	449
R1 ($I > 2\sigma(I)$)	0.085 (4051 obsd reflns)	0.046 (4705 obsd reflns)
wR2	0.230 (all data)[a]	0.106 (all data)[b]
GOF	1.06 (all data)	1.02 (all data)

[a] $w = 1/[\sigma^2(F_o^2) + (0.1242P)^2 + 2.8124P]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 2.7123P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Bis(phosphonium) Dichloride 7b (α- and *β*-Atropisomers). The mixture was prepared by a procedure corresponding to that used for **7a**, except the product is insoluble in $CHCl_3$ and the final reaction yellow residue was triturated with hot ^{i}PrOH. The resulting yellow suspension was filtered, washed with ^{i}PrOH (2 × 2 mL), and dried overnight under vacuum (305 mg, 83%). Anal. Calcd for $C_{32}H_{50}Cl_2O_5P_2$: C, 59.35; H, 7.78. Found: C, 59.73; H, 7.95. UV−vis: 242, 288, 360 nm.

Compound 7b-α. $^{31}P\{^1H\}$ NMR: *δ* 45.1 (s, P^1), 42.3 (s, P^2). ^1H NMR: *δ* 9.61 (s, 1H, H^1), 7.94 (s, 1H, H^3), 7.04 (d, $^3J_{HH}$ = 8.2, 1H, $H^{13'}$), 6.99 (br pseudo-d, $^3J_{HH}$ = 8.2, 1H, $H^{12'}$), 6.77 (d, $^3J_{HH}$ = 8.3, 1H, $H^{9'}$), 6.73 (s, 1H, H^8), 6.57 (d, $^3J_{HH}$ = 8.3, 1H, $H^{8'}$), 6.49 (s, 1H, H^{12}), 4.01 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx$ 13, 1H, H^4 ($^1H\{^{31}P\}$: d, $^3J_{HH}$ = 12)], 3.77 (s, 3H, OCH_3^9), 3.54 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx$ 13, 1H, H^6 ($^1H\{^{31}P\}$: d, $^3J_{HH}$ = 12)], 3.45 (s, 3H, OCH_3^{13}), 3.11 (br m, 1H, H^5), 2.59 (br m, 1H, $H^{5'}$), 2.53−2.32 (m, 6H, $P^1CH_2CH_3$), 2.32−2.17 (m, 6H, $P^2CH_2CH_3$), 1.25 (dt, $^2J_{PH}$ = 18.4, $^3J_{HH}$ = 7.5, 9H, $P^1CH_2CH_3$), 1.11 (dt, $^2J_{PH}$ = 18.1, $^3J_{HH}$ = 7.6, 9H, $P^2CH_2CH_3$). $^{13}C\{^1H\}$ NMR: *δ* 199.0 (s, C^1), 161.9 (d, $^3J_{PC}$ = 7.6, C^3), 150.0 (s, C^{10}), 148.4 (d, $^4J_{PC}$ = 1.5, C^{13}), 147.7 (s, C^9), 146.4 (d, $^4J_{PC}$ = 3.1, C^{14}), 126.3 (d, $^2J_{PC}$ = 6.1, C^2), 125.8 (s, $C^{8'}$), 124.9 (s, C^7), 120.6 (d, $^2J_{PC}$ = 5.4, C^{11}), 119.4 (d, $^4J_{PC}$ = 3.8, $C^{12'}$), 116.5 (d, $^4J_{PC}$ = 2.3, $C^{13'}$), 115.9 (s, $C^{9'}$), 115.5 (d, $^3J_{PC}$ = 5.4, C^{12}), 114.2 (s, C^8), 56.0 (s, OCH_3^9), 55.3 (s, OCH_3^{13}), 35.7 (dd, $^1J_{PC}$ = 45.1, $^3J_{PC}$ = 13.0, C^6), 28.6 (dd, $^1J_{PC}$ = 45.9, $^3J_{PC}$ = 13.8, C^4), 24.3 (s, C^5), 12.1 (d, $^1J_{PC}$ = 45.9, $P^1CH_2CH_3$), 10.5 (d, $^1J_{PC}$ = 47.4, $P^2CH_2CH_3$), 5.6 (d, $^2J_{PC}$ = 5.4, $P^1CH_2CH_3$), 5.0 (d, $^2J_{PC}$ = 5.4, $P^2CH_2CH_3$).

Compound 7b-*β*. $^{31}P\{^1H\}$ NMR: *δ* 44.9 (s, P^1), 42.4 (s, P^2). ^1H NMR: *δ* 9.61 (s, 1H, H^1), 8.00 (s, 1H, H^3), 6.92 (s, 1H, H^{12}), 6.77 (d, $^3J_{HH}$ = 8.2, 1H, $H^{9'}$), 6.73 (s, 1H, H^8), 6.53 (d, $^3J_{HH}$ = 8.2, 1H, $H^{8'}$), 6.36 (d, $^3J_{HH}$ = 7.9, 1H, $H^{13'}$), 6.31 (br pseudo-d, $^3J_{HH}$ = 7.9, 1H, $H^{12'}$), 3.95 (br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx$ 13, 1H, H^4, overlapping with OCH_3^{13}), 3.91 (s, 3H, OCH_3^{13}), 3.79 (s, 3H, OCH_3^9), 3.52 [br pseudo-t, $^2J_{PH} \approx {}^3J_{HH} \approx$ 13, 1H, H^6 ($^1H\{^{31}P\}$: d, $^3J_{HH}$ = 12)], 3.03 (br m, 1H, H^5), 2.64 (br m, 1H, $H^{5'}$), 2.51−2.32 (m, 6H, $P^1CH_2CH_3$), 2.32−2.17 (m, 6H, $P^2CH_2CH_3$), 1.26 (dt, $^2J_{PH}$ = 18.4, $^3J_{HH}$ = 7.5, 9H, $P^1CH_2CH_3$), 1.11 (dt, $^2J_{PH}$ = 18.1, $^3J_{HH}$ = 7.6, 9H, $P^2CH_2CH_3$). $^{13}C\{^1H\}$ NMR: *δ* 198.9 (s, C^1), 162.1 (d, $^3J_{PC}$ = 6.9, C^3), 149.7 (s, C^{10}), 148.7 (s, C^{13}), 147.9 (s, C^9), 146.7

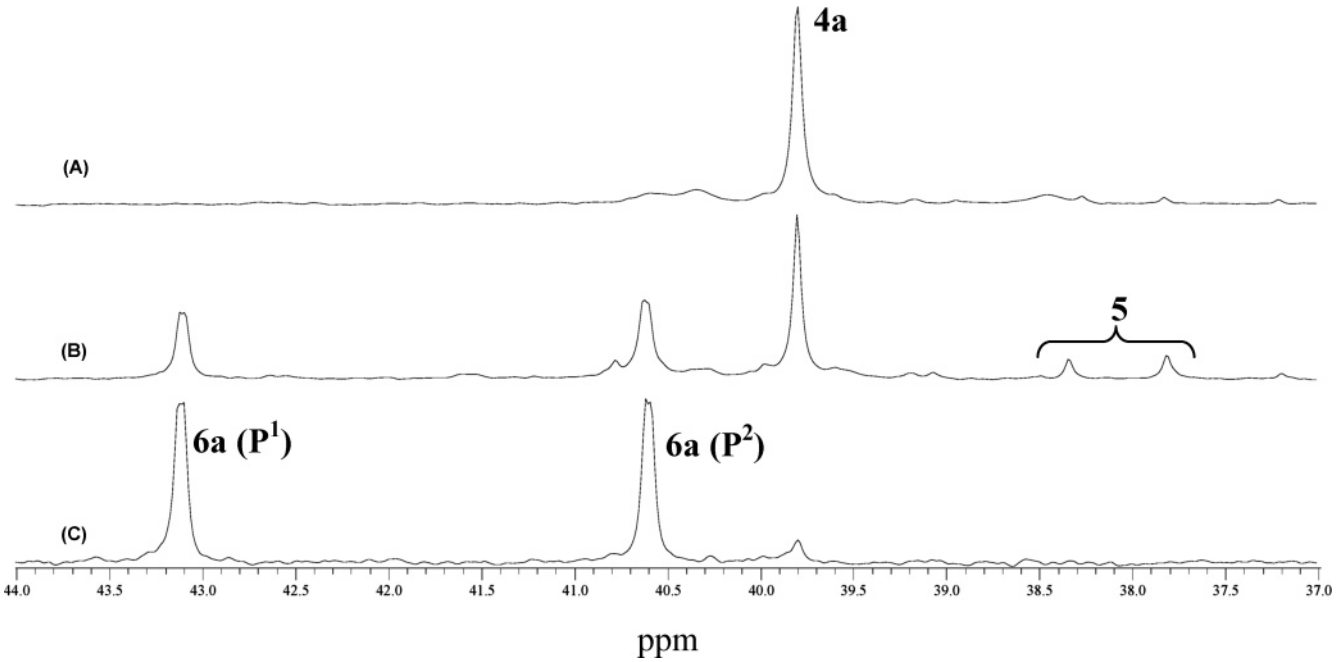


Figure 1. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of **1a** and Et_3P (1:1, H_2O, Ar, RT): (A) after 10 min, (B) after 3 h, and (C) after 2 days. See Scheme 1, where for **5** in this system, X = Y = OMe and R = R′ = Et.

(s, C^{14}), 127.2 (d, $^2J_{PC}$ = 6.1, C^2), 126.0 (s, $C^{12'}$), 125.1 (s, $C^{8'}$), 125.0 (s, C^7), 120.0 (d, $^2J_{PC}$ = 5.4, C^{11}), 116.4 (s, $C^{13'}$), 115.7 (s, $C^{9'}$), 114.2 (s, C^8), 109.4 (s, C^{12}), 56.5 (s, $OCH_3{}^{13}$), 56.1 (s, $OCH_3{}^9$), 35.9 (dd, $^1J_{PC}$ = 44.4, $^3J_{PC}$ = 13.0, C^6), 28.4 (dd, $^1J_{PC}$ = 45.9, $^3J_{PC}$ = 13.8, C^4), 24.3 (s, C^5), 12.2 (d, $^1J_{PC}$ = 45.9, $P^1CH_2CH_3$), 10.6 (d, $^1J_{PC}$ = 47.4, $P^2CH_2CH_3$), 5.7 (d, $^2J_{PC}$ = 5.4, $P^1CH_2CH_3$), 5.0 (d, $^2J_{PC}$ = 5.4, $P^2CH_2CH_3$).

Bis(phosphonium) Dichloride 7c. The salt was prepared by the procedure used for **7b**, although the product was now a pale yellow solid (125 mg, 67%).

Bis(phosphonium) Dichloride 7d. The salt was prepared by a procedure corresponding to that used to obtain **7a**, but after being dried under vacuum overnight, the yellow residue was triturated with hot ^{i}PrOH; the suspension of **7d** was filtered, washed with ^{i}PrOH, and dried under vacuum at ~60 °C for 4 h (105 mg, 70%). A sample was recrystallized from EtOH and dried under vacuum at 80−90 °C for 2 h

Bis(phosphonium) Dichlorides 7e−g. These materials were synthesized as non-purified yellow powders by the procedure described for **7a**. Purification proved to be difficult because of decomposition or insolubility of the materials in $CHCl_3$.

Spectroscopic and analytical data for the bis(phosphonium chlorides) compounds **7d−g** are given in Table S2.

NMR Investigation of the Reaction of Et_3P with Sinapaldehyde (1a). Et_3P (17.6 mg, 0.15 mmol) was added under Ar to a suspension of the aldehyde (31 mg, 0.15 mmol) in air-free D_2O (~2 mL). After the compounds had dissolved (~10 min), the solution (~0.7 mL) was placed into a J-Young NMR tube, and NMR spectra were recorded periodically (see text). ^1H NMR (300 MHz) for **4a**: δ 6.60 (d, $^4J_{PH}$ = 3.0, 2H, C_6H_2), 4.88 (s, 1H, $CH(OD)_2$), 3.78 (s, 6H, OCH_3), 3.67 (d, $^2J_{PH}$ = 15.4, 1H, PC*H*), 2.27−2.10 (m, 6H, PCH_2), 1.24−1.06 (m, 9H, PCH_2CH_3). For **6a**: δ 9.36 (s, 1H, H^1), 7.75 (s, 1H, H^3), 6.62 (s, 1H, H^{12}), 6.51 (s, 2H, $H^{8,8'}$), 6.11 (s, 1H, $H^{12'}$), 4.04 [d, $^2J_{PH}$ = 15.6, 1H, H^4 ($^1H\{^{31}P\}$: s)], 3.80 (s, 3H, $OCH_3{}^{13}$), 3.54 (s, 6H, $OCH_3{}^{9,9'}$), 3.38 [d, $^2J_{PH}$ = 15.6, 1H, H^6 ($^1H\{^{31}P\}$: s], 3.17 (s, 3H, $OCH_3{}^{13'}$), 2.40−2.06 (m, 12H, PCH_2), 1.27−0.96 (m, 18H, PCH_2CH_3). $^2D\{^1H\}$ NMR (H_2O) for **6a**: δ 3.17 (br s, D^5), 2.48 (br s, $D^{5'}$). $^{31}P\{^1H\}$ NMR data (see text) were similarly monitored for the same reaction carried out in H_2O.

NMR Investigation of the Reaction of ^{i}Pr$_3$P with 1a. The procedure used was as above, except that 8 mg of ^{i}Pr$_3$P (0.05 mmol) and 10 mg of **1a** (0.05 mmol) were used (the phosphine did not dissolve completely). NMR spectra were recorded after 2 h. For **4h** $^{31}P\{^1H\}$ NMR: δ 41.3 s. ^1H NMR: δ 6.73 (d, $^4J_{PH}$ = 1.7, 2H, C_6H_2), 4.81 (s, 1H, $CH(OD)_2$, overlapping with *H*OD resonance), 3.95 [d, $^2J_{PH}$ = 15.7, 1H, PC*H*(Ph), ($^1H\{^{31}P\}$: s)], 3.84 (s, 6H, OCH_3), 2.98−2.80 (m, 3H, PC*H*), 1.47−1.27 (m, 18H, CH_3). $^{13}C\{^1H\}$ NMR (after 2 days): δ 89.3 (d, $^3J_{PC}$ = 15, $CH(OD)_2$), 58.0 (s, OCH_3), 36.1 (d, $^1J_{PC}$ = 40, P*C*H(Ph)), 22.0 (d, $^1J_{PC}$ = 40, P*C*H), 17.8 and 17.7 (two d, $^2J_{PC}$ = 4, CH_3). For **3h** $^{31}P\{^1H\}$ NMR: δ 42.3 s. ^1H NMR: δ 9.58 (br s, 1H, C*H*O), 4.52 [br d, $^2J_{PH}$ = 14.4, 1H, PC*H*(Ph) ($^1H\{^{31}P\}$: s)].

NMR Investigation of the Reaction of Ph_2PMe with 1a. The above procedure was followed, except that 10 mg of Ph_2PMe (0.05 mmol) and 10 mg of **1a** (0.05 mmol) were used, and again the phosphine did not dissolve completely. NMR spectra were recorded after 1 day. For **4i** $^{31}P\{^1H\}$ NMR: δ 26.1 s. ^1H NMR: δ 7.96−7.52 (m, 10H, C_6H_5), 6.32 (d, $^4J_{PH}$ = 2.3, 2H, C_6H_2), 4.85 (s, 1H, $CH(OD)_2$), 4.52 [d, $^2J_{PH}$ = 15.8, 1H, PC*H* ($^1H\{^{31}P\}$: s)], 3.62 (s, 6H, OCH_3), 2.33 (d, $^2J_{PH}$ = 13.4, 3H, PCH_3). For **3i** $^{31}P\{^1H\}$ NMR: δ 26.7 s.

X-ray Crystallographic Analyses of 7a and 7d. X-ray quality, prism crystals of the pale yellow **7a**·2^{i}PrOH and yellow **7d**·EtOH·H_2O were obtained by crystallization from saturated solutions of **7a** and **7d** in ^{i}PrOH and EtOH, respectively. Selected crystallographic data for the dichlorides are shown in Table 1, and more details are provided in the Supporting Information. Measurements were made at 173 (±0.1) K on a Rigaku/ADSC (for **7a**) or a Bruker X8 APEX diffractometer (for **7d**) using graphite-monochromated Mo Kα radiation (0.71073 Å). Data (given as **7a**/**7d**) were collected to a maximum 2θ value of 45.1/50.5°, in a series of ϕ and ω scans in 0.50° oscillations with 31.0/10.0 s exposures; the crystal-to-detector distance was 39.00/35.98 mm. Of the 16 023/25 943

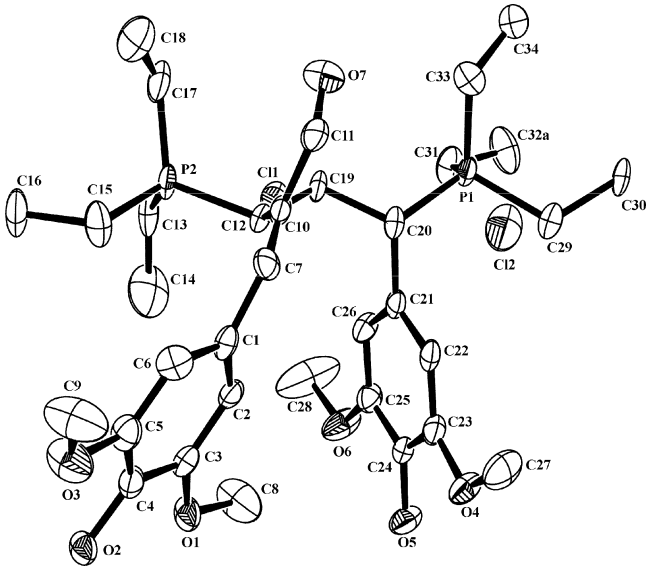


Figure 2. ORTEP diagram of **7a** (*S*,*S*-diastereomer) showing 50% probability thermal ellipsoids; H-atoms omitted for clarity.

reflections collected, 5964/6455 were unique (R_{int} = 0.073/0.047); equivalent reflections were merged. Data for **7a** were collected using the d*TREK software package,[9] processed using TwinSolve,[10] and corrected for absorption effects using a multiscan technique (TwinSolve), with normalized minimum and maximum transmission coefficients of 0.522 and 0.982, respectively. For **7d**, data were collected and integrated using the Bruker SAINT software package[11] and were corrected for absorption effects using the multiscan technique (SADABS)[12] with minimum and maximum transmission coefficients of 0.808 and 0.924, respectively. Both sets of data were corrected for Lorentz and polarization effects, and the structures were solved by direct methods.[13] Within **7a**, one ethyl substituent is disordered and was modeled in two orientations; within **7d**, the EtOH molecule is disordered and one MeO substitutent is disordered over two sites. The hydroxyl hydrogens of the aromatic rings and the two ^{i}PrOH solvate molecules of **7a** were located in a difference map but were refined using the SHELXL HFIX 147 command. All the OH hydrogen atoms of **7d** (including those of the solvates) were located in difference maps and refined isotropically. All other hydrogen atoms of the structures were included in calculated positions but not refined.

Results and Discussion

Scheme 1 shows a summary of the reactions of sinapaldehyde (**1a**), coniferylaldehyde (**1b**), and coumaraldehyde (**1c**) with a range of tertiary phosphines, of which Et_3P was first tested. Scheme 1 also lists the $^{31}P\{^1H\}$ data for intermediates **3a** and **4a,** as well for **6a**; corresponding data are also given for the other aldehyde−phosphine systems (see below). Mixing of the slightly water-soluble **1a** and Et_3P in a 1:1 ratio in water under Ar at room temperature (RT) generated over 10 min an orange and then red solution, which gave a sharp $^{31}P\{^1H\}$ signal at δ_P 39.8 (Figure 1A), the region associated with phosphonium resonances.[14] A ^1H NMR investigation of the reaction in D_2O showed that this ^{31}P signal is associated with the zwitterion **4a**, which is formed after nucleophilic attack of the phosphine on the γ-carbon of the propenoid chain of **1a** (the C-atoms are labeled as shown in Scheme 2). All the ^1H resonances of **1a** had disappeared, and a singlet at δ_H 4.88 (from the α-proton of the diol **4a**) and a doublet at δ_H 3.67, which becomes a singlet in the $^1H\{^{31}P\}$ spectrum ($^2J_{PH}$ = 15.4 Hz) attributable to the γ-proton, are generated; the β-protons of **4a** are not seen because of fast H/D-exchange. An analogous ^1H pattern has been observed for the corresponding phosphonium derivative formed from cinnamaldehyde and $[HO(CH_2)_3]_3P$,[3] but the presence of the *p*-OH group stabilizes **4a** compared with the corresponding intermediate in the cinnamaldehyde reaction. The position of the α-proton signal indicates that **4a** exists mostly as the diol rather than as the aldehyde form, **3a**, which, nevertheless, was detected within 10 min of the reaction by a broadened singlet at δ_P 40.6 (**4a**/**3a** ≈ 10), the aldehyde proton appearing as a small broad singlet at δ_H 9.56.

Table 2. Selected Bond Distances and Angles for **7a** with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
C(20)−P(1)	1.816(6)	C(21)−C(20)−P(1)	112.9(4)
C(12)−P(2)	1.837(6)	C(19)−C(20)−P(1)	112.1(4)
C(29)−P(1)	1.805(6)	C(10)−C(12)−P(2)	112.4(4)
C(31)−P(1)	1.793(7)	C(19)−C(12)−P(2)	110.4(4)
C(33)−P(1)	1.819(7)	O(7)−C(11)−C(10)	128.3(6)
C(11)−O(7)	1.201(7)	C(7)−C(10)−C(11)	115.9(6)
C(11)−C(10)	1.463(9)	C(7)−C(10)−C(12)	125.9(6)
C(10)−C(7)	1.309(8)	C(10)−C(7)−C(1)	132.0(6)
C(7)−C(1)	1.476(9)	C(20)−P(1)−C(29)	105.9(3)
		C(20)−P(1)−C(31)	111.5(3)
		C(20)−P(1)−C(33)	106.7(3)
		C(12)−P(2)−C(13)	107.8(3)
		C(12)−P(2)−C(15)	107.5(3)
		C(12)−P(2)−C(17)	114.8(3)

Compound **4a** cannot be isolated because it slowly undergoes self-condensation to give the isolable **6a**; the process is considered to occur via the carbanion site of **2** and involves loss of a water molecule and migration of one Et_3P group (Scheme 1); two low-intensity $^{31}P\{^1H\}$ signals seen at δ_P 38.3 and 37.8 may be associated with the required intermediate **5** (Figure 1B). The "double" zwitterionic **6a** is fully formed as a deep red solution (because of a strong absorption at 450 nm) over 3 days at RT (or 3 h at 50 °C) and is isolated as an almost black solid.

The $^{31}P\{^1H\}$ spectrum of **6a** shows two doublets at δ_P 43.1 and 40.6 ($^4J_{PP}$ = 3 Hz) associated, respectively, with P^1 and P^2 atoms (Figure 1C), which show correlation in a $^{31}P\{^1H\}-^{31}P\{^1H\}$ COSY experiment. It should be noted here that

(9) *d*TREK, Area Detector Software*, version 4.13; Molecular Structure Corporation: The Woodlands, TX, 1996−1998.
(10) *CrystalClear*, version 1.3.6; Rigaku: The Woodlands, TX, 2004.
(11) *SAINT*, version 7.03A; Bruker AXS Inc.: Madison, WI, 1997−2003.
(12) *SADABS, Bruker Nonius area detector scaling and absorption correction*, version 2.10; Bruker AXS Inc.: Madison, WI, 2003.
(13) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.
(14) (a) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Weinheim, Germany, 1987; Chapter 1. (b) Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Weinheim, Germany, 1987; Chapter 2. (c) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley-Interscience: New York, 2000; Chapter 6. (d) Moiseev, D.; James, B. R.; Patrick, B. O.; Hu, T. *Inorg. Chem.* **2006**, *45*, 2917.

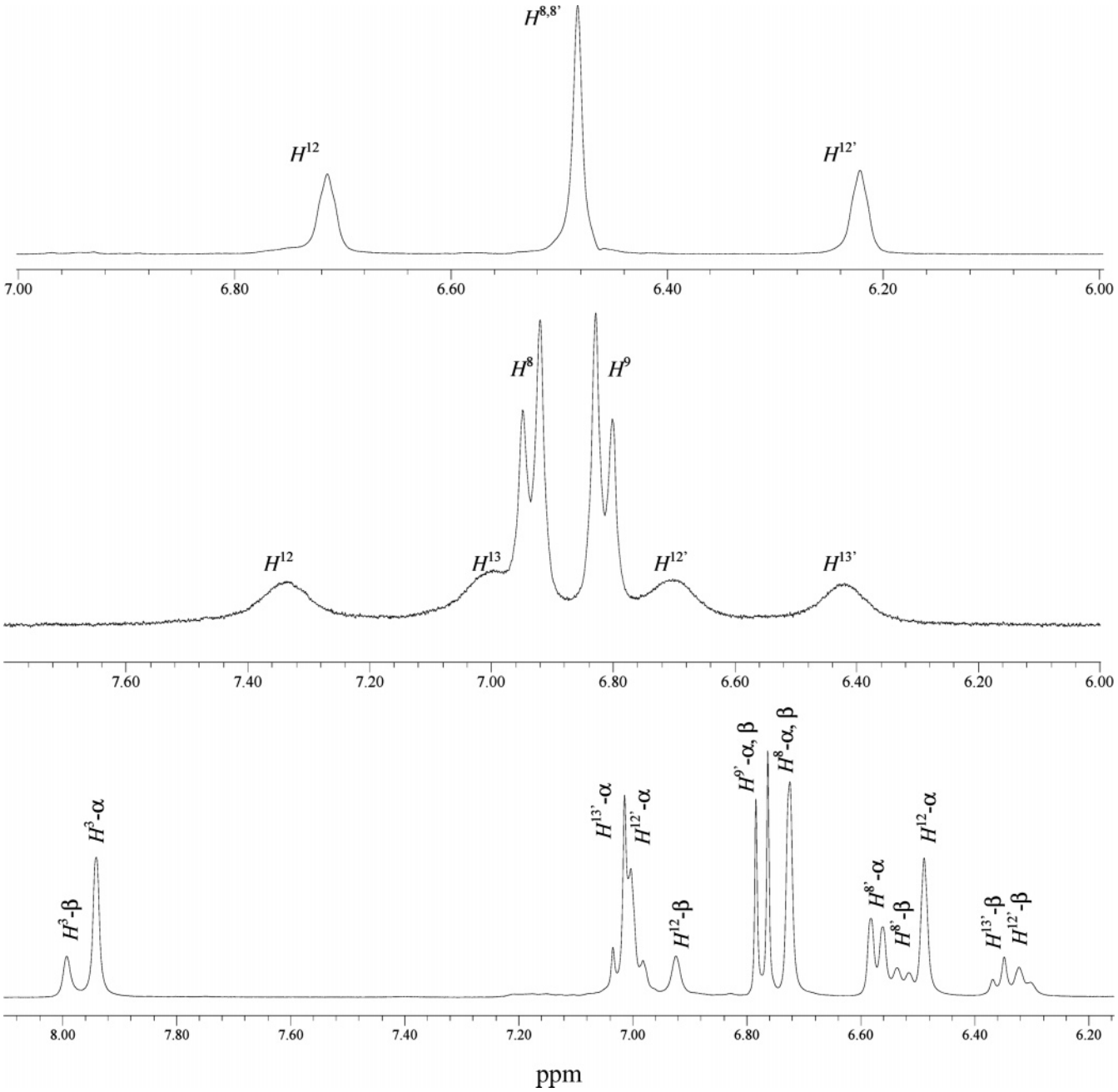


Figure 3. Aromatic region of the ^{1}H NMR spectrum in D_2O of (A) **7a**, (B) **7c**, and (C) **7b**.

although compounds **6a**−**g** and **7a**−**g** possess chiral centers at C^4 and C^6, the relative simplicity of the NMR data are consistent with the presence of just two enantiomers in each case, implying stereoselectivity in the self-condensation process, including migration of the phosphonium moiety within **5**. Of note, the X-ray structural analysis of **7a** and **7d** (see below) support in each case the presence of just the *R*,*R*- and *S*,*S*-enantiomers. Detailed ^{1}H NMR data are fully consistent with the formulation of **6a**. The H^1 and H^3 protons appear as singlets at δ_H 9.30 and 7.67, respectively (the corresponding proton signals of **1a** appear at δ_H 9.50 and 7.62). The diastereotopic (anisochronous) H^5 and $H^{5'}$ protons are seen as broad multiplets at δ_H 3.19 and 2.48, respectively ($\Delta\delta$ = 0.71 ppm), both resonances correlating with one carbon C^5 resonance at δ_C 24.6 (s) in a ^{1}H−^{13}C{^{1}H} HSQC experiment; in a ^{1}H{^{31}P} spectrum, each resonance appears as a broad pseudo-triplet instead of the expected triplet of doublets. The H^4 and H^6 protons appear as pseudo-triplets at δ_H 3.98 and 3.36, respectively; in the ^{1}H{^{31}P} spectrum, these protons each appear as a broad pseudo-doublet that must result from coupling to the diastereotopic H^5 and $H^{5'}$ protons. The ^{1}H spectrum of the product of the reaction carried out in D_2O revealed the same resonances except for those of H^5 and $H^{5'}$, which are completely replaced by deuterons, the latter appearing in the ^{2}D{^{1}H} spectrum as broad singlets at δ_D 3.17 and 2.48; this type of exchange has been discussed previously for the cinnamaldehyde system[3] and must occur via the carbanion site of intermediate **2**. The ^{1}H and ^{13}C{^{1}H} spectra reveal restricted rotation of the aromatic ring **B**. The aromatic protons H^{12} and $H^{12'}$ appear

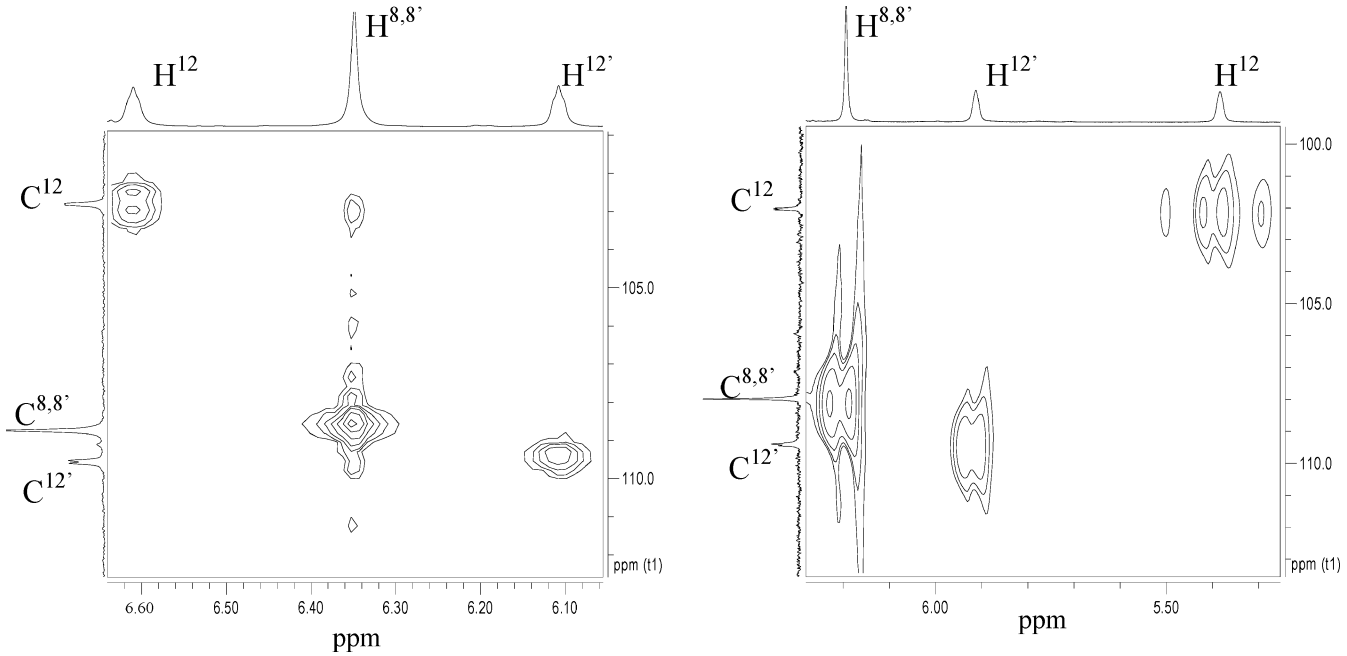


Figure 4. $^1H-^{13}C\{^1H\}$ (HMQC) NMR spectrum in the aromatic region of **7a** (left) and the $^1H-^{13}C\{^1H\}$ (HSQC) NMR spectrum in the aromatic region of **7f** (right) in D_2O.

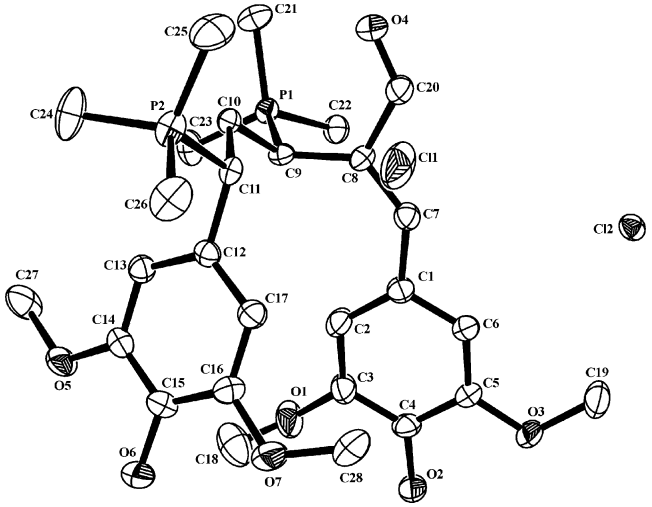


Figure 5. ORTEP diagram of **7d** (*R,R*-diastereomer) showing 50% probability thermal ellipsoids; H-atoms omitted for clarity.

as singlets at δ_H 6.61 and 6.09, respectively, and correlate in a $^1H-^1H$ COSY experiment, and the corresponding C^{12} and $C^{12'}$ atoms appear as doublets at δ_C 104.3 ($^3J_{PC} = 3.1$ Hz) and 111.2 ($^3J_{PC} = 6.1$ Hz), respectively; for ring **A**, there is just one singlet at δ_H 6.45 for the equivalent H^8 and $H^{8'}$ protons. In an NOE experiment, the H^3 proton (δ_H 7.67) correlates with these protons and with H^1 (δ_H 9.30). Similarly, separate ^1H and $^{13}C\{^1H\}$ signals are seen for each of the MeO groups of ring **B** but not of ring **A** (see Experimental Section), while in an NOE experiment the resonances of the H^{12} and $H^{12'}$ protons and these MeO groups appear in the same phase, confirming attachment to a rotationally hindered ring **B**.

The bis(zwitterionic) **6b**, formed by reaction of coniferylaldehyde (**1b**) with Et_3P, gives a $^{31}P\{^1H\}$ spectrum showing singlets with shoulders at δ_P 44.6 and 41.8, associated with the P^1 and P^2 atoms, respectively, and the ^1H and $^{13}C\{^1H\}$ spectra reveal the presence of two atropisomers. The NMR spectra of **6b** are discussed below with those of the derived dichloride **7b** where the resonances of the two isomers are better resolved.

Coumaraldehyde (**1c**) reacts with Et_3P in the same manner as does sinapaldehyde and yields the corresponding bis(zwitterionic) **6c**; Scheme 1 gives the $^{31}P\{^1H\}$ data. In the ^1H spectrum, the H^5 and $H^{5'}$ protons are anisochronous by 0.66 ppm, and the aromatic protons of ring **B** appear as broad, unresolved singlets, while the C^{12} and $C^{12'}$ atoms also appear as broad singlets at δ_C 127.5 and 133.7, respectively, in the $^{13}C\{^1H\}$ spectrum.

Although compounds **6a**−**c** have well-resolved NMR spectra, they always contain some impurities, the major one being the phosphine oxide Et_3PO (up to 5%), which could be formed either by oxidation of Et_3P by hydroxide,[15] or more likely, by oxidation of an Et_3P moiety in the presence of base with concomitant reduction of the associated C-atom as we have demonstrated for a cinnamaldehyde system.[3] Moreover, these phenolic compounds are possibly isolated from the aqueous solutions as a mixture of the zwitterionic form and the corresponding protonated phosphonium salts with OH^- as the counterion. We have thus been unable to obtain satisfactory elemental analyses for **6a**−**c**. However, treatment of these dark, almost black compounds with aqueous HCl yields the corresponding dichloride salts **7a**−**c**, and these were purified by crystallization from $CHCl_3$ or by trituration with hot ^{i}PrOH. An X-ray quality, pale yellow crystal of **7a** was obtained by crystallization from a saturated solution of the compound in ^{i}PrOH. The molecular structure is shown in Figure 2, and selected geometrical parameters are given in Table 2. The compound crystallizes as a mixture of *S,S*- and *R,R*-enantiomers, which is consistent with the

(15) Bloom, S. M.; Buckler, S. A.; Lambert, R. F.; Merry, E. V. *J. Chem. Soc. D, Chem. Commun*. **1970**, 870.

Table 3. Selected Bond Distances and Angles for **7d** with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
C(9)−P(1)	1.815(2)	C(12)−C(11)−P(2)	109.51(16)
C(11)−P(2)	1.804(2)	C(10)−C(11)−P(2)	112.26(16)
C(24)−P(2)	1.773(3)	C(8)−C(9)−P(1)	113.22(17)
C(25)−P(2)	1.769(3)	C(10)−C(9)−P(1)	110.51(16)
C(26)−P(2)	1.771(3)	O(4)−C(20)−C(8)	125.4(3)
C(20)−O(4)	1.203(3)	C(7)−C(8)−C(20)	114.2(2)
C(8)−C(20)	1.462(4)	C(7)−C(8)−C(9)	127.5(2)
C(7)−C(8)	1.341(3)	C(8)−C(7)−C(1)	136.8(2)
C(7)−C(1)	1.453(3)	C(9)−P(1)−C(21)	109.93(12)
		C(9)−P(1)−C(22)	112.11(12)
		C(9)−P(1)−C(23)	106.48(12)
		C(11)−P(2)−C(24)	109.77(13)
		C(11)−P(2)−C(25)	111.10(13)
		C(11)−P(2)−C(26)	108.46(13)

Table 4. Selected ^{1}H NMR Data for Products Formed from Sinapaldehyde and Tertiary Phosphines

	chemical shift, ppm					
product	H^{12}	$H^{12'}$	$\Delta(H^{12}-H^{12'})$	H^5	$H^{5'}$	$\Delta(H^5-H^{5'})$
6a	6.61	6.09	0.52	3.19	2.48	0.71
6d	6.55	6.02	0.53	3.11	2.52	0.59
6e	6.65	6.15	0.50	3.25	2.58	0.67
6f	5.39	5.94	−0.55	3.17	2.01	1.16
6g	5.08	6.00	−0.92	3.19	1.81	1.38
7a	6.71	6.21	0.50	3.12	2.70	0.42
7d	6.58	6.02	0.56	2.91	2.74	0.17
7e	6.69	6.20	0.49	3.08	2.77	0.31
7f	5.39	5.92	−0.53	3.12	2.21	0.91
7g	5.17	6.12	−0.95	3.14	2.12	1.02

two $^{31}P\{^1H\}$ singlets seen in solution at δ_P 45.0 and 42.5 for P^1 and P^2 atoms, respectively; similar enantiomers are presumed to be present in **6a**. The P atoms in **7a** exhibit normal tetrahedral coordination with C−P−C angles in the range of 105.9−114.8°. Ring **A** is not coplanar with the planar, conjugated system defined by the C1−C4 atoms in Scheme 1 (atoms C11, C10, C7, and C19 in Figure 2); in the corresponding structure containing $[Me_3P-C]^+$ groups (see **7d** below), ring **A** does exhibit this coplanarity. The reason for the difference is unclear, but both structures are replete with hydrogen-bond interactions involving the chloride anions, the phenolic-OH groups, and the solvate molecules (^{i}PrOH in **7a**, and EtOH and H_2O in **7d**), and these likely play a role.

As for **6a**, the ^{1}H NMR spectrum of **7a** reveals singlets for each of the $H^{12}/H^{12'}$ protons and for each of the ring **B**-MeO substitutents and just one singlet for H^8 and $H^{8'}$ (Figure 3A), and there are appropriate, corresponding $^{13}C\{^1H\}$ signals. The ^{1}H signals were assigned on the basis of $^1H-^{13}C\{^1H\}$ (HSQC) data, and such an experiment revealed that the upfield-shifted C^{12}-carbon correlates with the downfield-shifted H^{12}-proton (Figure 4). The H^5 and $H^{5'}$ protons of **7a** are anisochronous by 0.42 ppm, compared with the $\Delta\delta$ value of 0.71 seen for **6a**. The NMR spectrum of **7a** in CD_3OD (vs D_2O) shows better resolution for the H^4, H^5, $H^{5'}$, and H^6 protons, and the signals appear in the $^1H\{^{31}P\}$ spectrum as an X−AB−Y spin system simulated by the parameters: $\Delta\delta_{AB} = 0.233$ ppm, $J_{AB} = 13$, $J_{AX} = J_{BY} = 12$, $J_{AY} = J_{BX} = 2$, and $J_{XY} = 0$ Hz; in CD_3OD, however, **7a** slowly decomposes.

In Scheme 1, species **6** and **7** are written, respectively, with the two phenolic-OH groups either fully deprotonated or fully protonated, and this seems reasonable considering their methods of synthesis. However, in H_2O/D_2O, the systems will involve both forms in rapid equilibrium, depending on the pK_a values, and the NMR shifts are likely an average of the species present, the values depending on the relative concentrations of the species. The aqueous solutions were not buffered (since the presence of extraneous salts would certainly complicate the studies), and the pK_a values for these zwitterionic systems have not been determined. Nevertheless, the formulations are considered essentially correct, as judged by differences in the $^{13}C\{^1H\}$ data for the *C*−OH atoms and by the UV−vis data. For example, $\delta(C^{10}) = 150.8$ and 139.5 for **6a** and **7a**, respectively, and the corresponding $\delta(C^{14})$ values are 144.5 and 135.3, data that are consistent with attachment to O^- and OH, respectively; the UV−vis data ($\lambda_{max} = 450$ and 360 nm for **6a** and **7a**, respectively) are also typical of deprotonated and protonated forms of phenol derivatives.[16]

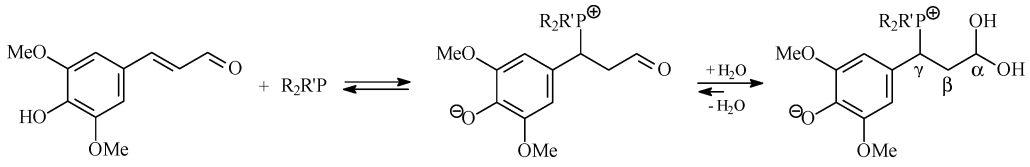
The ^{1}H spectrum of **7c** (X = Y = H, see Scheme 1) reveals four signals for ring **B** (Figure 3B): H^{12} and $H^{12'}$ at δ_H 7.34 and 6.70, and H^{13} and $H^{13'}$ at δ_H 7.00 and 6.41, respectively. The $^{13}C\{^1H\}$ spectrum shows C^{12} and $C^{12'}$ as broad singlets at δ_C 129.1 and 135.1, respectively, although C^{13} and $C^{13'}$ appear as one signal at δ_C 118.2.

In the reaction of Et_3P with coniferylaldehyde (**1b**), where the aromatic ring is unsymmetrical, two atropisomers (**7b-α** and **7b-*β***) are formed in a 3:1 ratio, as seen by ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. This isomerism presumably arises because of restricted rotation of ring **B**, in which the MeO group can be located in two ways (cf., Figures 2 and 5), the favored situation being when the OMe groups of rings **A** and **B** point towards the outside of the molecule (called isomer **7b-α**); this isomer shows $^{31}P\{^1H\}$ singlets at δ_P 45.1 and 42.3 for P^1 and P^2, respectively, while **7b-*β*** (where the MeO is directed towards ring **A**) is associated with singlets at δ_P 44.9 and 42.4. The proton shifts for H^1, H^8 and $H^{9'}$ are the same for both isomers, and there are minor differences for H^3 (δ_H 7.94 and 8.00 for **7b-α** and **7b-*β***, respectively) and $H^{8'}$ (δ_H 6.57 and 6.53), but more significant differences are seen for the ring **B** protons (Figure 3C). In **7b-α**, the H^{12} signal (δ_H 6.49) is upfield-shifted to those of $H^{12'}$ and $H^{13'}$ (δ_H 6.99 and 7.04), while the reverse is seen for **7b-*β*** (Figure 3C). The position of the MeO group affects also the shifts of the protons of the C^4-C^6 chain: the H^4 and H^6 signals of **7b-α** are at δ_H 4.01 and 3.54, respectively; the same protons of **7b-*β*** are slightly upfield-shifted (δ_H 3.95 and 3.52), and the $\Delta\delta$ value for the geminal H^5 and $H^{5'}$ protons is greater for **7b-α** (0.52 ppm) than that for **7b-*β*** (0.39 ppm).

The tertiary phosphines Me_3P, $[HO(CH_2)_3]_3P$, Me_2PPh, and Et_2PPh react with sinapaldehyde (**1a**) in the same manner as Et_3P and give the corresponding bis(zwitterionic) salts **6d**−**g**, which with HCl generate the respective dichlorides

(16) Ragnar, M.; Lindgren, C. T.; Nilvebrant, N-O. *J. Wood Chem. Technol.* **2000**, *20*, 277.

Scheme 2



			$^{31}P\{^1H\}$, ppm		$^{31}P\{^1H\}$, ppm
1a	R = R' = ^{i}Pr	**3h**	42.3	**4h**	41.3
	R = Ph; R' = Me	**3i**	26.7	**4i**	26.1
	R = Ph; R' = (*m*-SO_3-C_6H_4)Na	**3j**	-	**4j**	24.9 (trace)
	R = R' = *cyclo*-C_6H_{11}	**3k**	-	**4k**	31.9 (trace)

7d−**g** (Scheme 1), although **7f** and **7g** were unstable in alcohols and could not be purified. The structure of a yellow crystal of **7d**, obtained by crystallization from a saturated EtOH solution of the compound, was determined by X-ray analysis (Figure 5, Table 3), and like **7a**, the material was obtained as a mixture of *S,S*- and *R,R*-enantiomers. As for **6a** and **7a**, **6d**−**g** and **7d**−**g** also show restricted rotation of ring **B**.

The chemical shifts of the $H^{12,12'}$ and $H^{5,5'}$ protons of **6a**, **6d**−**g**, **7a**, and **7d**−**g**, derived from sinapaldehyde (Table

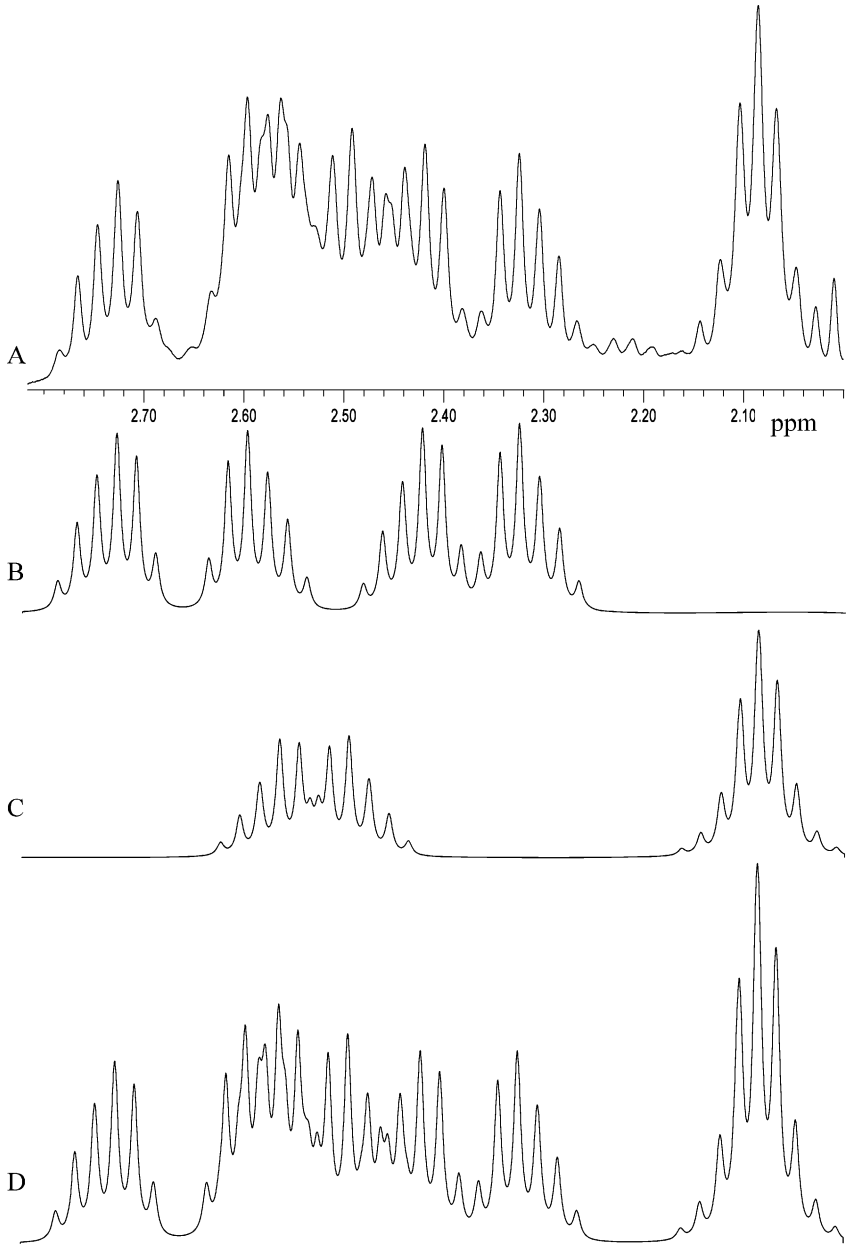


Figure 6. (A) Experimental $^1H\{^{31}P\}$ NMR spectrum for the P-CH_2 protons of the Et_2PPh derivative **7g** in D_2O. (B) Simulated ABX_3 spectrum of the P^1-CH_2 protons (J_{AB} = 16.0 and $J_{AX} = J_{BX}$ = 7.7 Hz). (C) Simulated spectrum of the P^2-CH_2 protons (J_{AB} = 16.0 and $J_{AX} = J_{BX}$ = 7.7 Hz). (D) Superimposition of spectra B and C. See the text for the selected chemical shift differences.

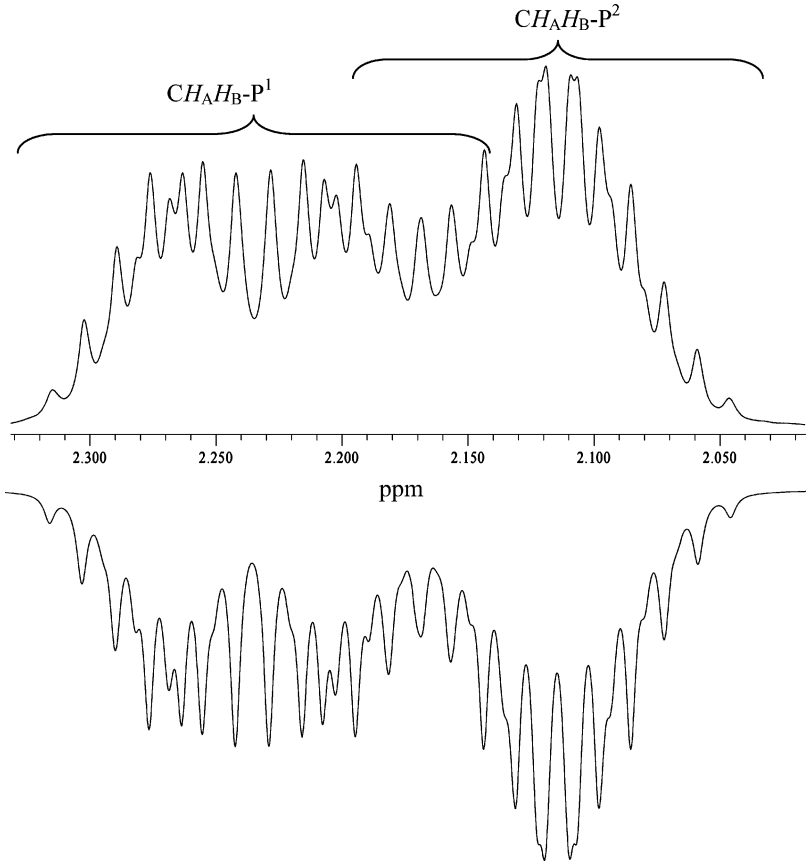


Figure 7. Experimental (top) and simulated (bottom) ^{1}H NMR spectra for the P-CH_2 protons of the Et_3P derivative **7a** in D_2O. There are two overlapping ABX_3Y spin systems with $J_{AB} = 16.0$, $J_{AX} = J_{BX} = 7.7$, and $J_{AY} = J_{BY} = 12.6$ Hz. See the text for the selected chemical shift differences.

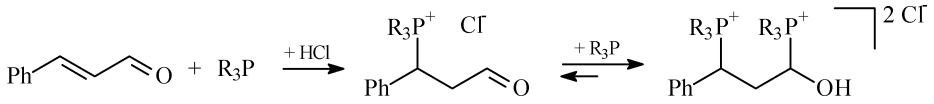
4), show two distinctive features (the H^{12} and C^{12} resonances were correlated by HSQC experiments, the C^{12} resonance always being upfield vs that of $C^{12'}$). First, for the **a**, **d**, and **e** species, containing solely alkyl-substituted phosphines, the C^{12} signal correlates with the more downfield-shifted proton (Figure 4, left) and $\Delta(H^{12}-H^{12'})$ is positive; for the Et_2PPh- and Me_2PPh-containing compounds (**f** and **g**), the C^{12} signal correlates with the upfield-shifted proton (Figure 4, right), and $\Delta(H^{12}-H^{12'})$ is negative (Table 4). It is possible that in the phenyl-containing phosphine systems the $H_{12}/H_{12'}$ protons experience some ring-current effect of the phenyl group. The $\Delta(H^{12}-H^{12'})$ values for the **a** and **d**−**f** species (∼0.50 ppm) are also noted to be about half those of the **g** species (∼0.95 ppm). Second, the degree of anisochronism of the geminal H^5 and $H^{5'}$ protons, equated with $\Delta(H^5-H^{5'})$, increases with the bulk of the phosphine, the smallest differences 0.59 and 0.17 ppm being observed for Me_3P derivatives **6d** and **7d**, respectively (Table 4); the Et_2PPh derivatives **6g** and **7g** show the largest $\Delta(H^5-H^{5'})$ values of 1.38 and 1.02 ppm, respectively, perhaps resulting from increased strain in the C^4-C^6 chain.

When the more bulky $^iPr_3P$ was reacted with **1a** (1:1, H_2O, RT, Ar), the self-condensation reaction did not occur. NMR data reveal an equilibrium between the zwitterions **3h** and **4h** (**4h**/**3h** ≈ 10), and a ^{1}H spectrum of the same reaction in D_2O provided a **1a**/(**3h** + **4h**) value of 2:3 (see Scheme 2). The α- and γ-protons of **4h** appear, respectively, as a singlet at δ_H 4.78 (close to the value seen for the Et_3P analogue **4a**) and a doublet (δ_H 3.95, $^2J_{PH} = 15.8$ Hz) that became a singlet in the $^1H\{^{31}P\}$ spectrum (∼0.3 ppm downfield from the value for **4a**). The aldehyde proton of **3h** appears as a broad singlet at δ_H 9.56, and the γ proton as a doublet at δ_H 4.06 ($^2J_{PH} =$ 12.0 Hz), while the β-protons (as for **4a**) cannot be seen because of H/D exchange. $^{13}C\{^1H\}$ data revealed the α- and γ-carbons of **4h** as doublets at δ_C 89.4 ($^3J_{PC} = 15.3$ Hz) and 36.1 ($^1J_{PC} = 39.8$ Hz), respectively. In the reaction of **1a** with $MePPh_2$, the **4i**/**3i** and **1a**/(**3i** + **4i**) ratios were 8 and 2, respectively; the γ-proton of **4i** is downfield-shifted (δ_H 4.52, $^2J_{PH} = 15.8$ Hz) because of the electron-withdrawing Ph groups. When $Na[Ph_2P(m\text{-}SO_3\text{-}C_6H_4)]$ or $(cyclo\text{-}C_6H_{11})_3P$ was reacted with **1a**, only trace amounts of a corresponding zwitterion (presumably of type **4**) were detected (Scheme 2). No reaction was observed between **1a** and $(NCCH_2CH_2)_3P$.

Like the methylene H^5 and $H^{5'}$ atoms adjacent to the C^4 and C^6 chiral centers, the P^1 and P^2 atoms of **6f**/**g** and **7f**/**g** are prochiral centers[17] and contain, respectively, two magnetically inequivalent, diastereotopic Me/Et substituents. Thus, for example, four methyl resonances are seen in the ^{1}H spectrum of **7f**: doublets at δ_H 2.50 and 2.20 ($^2J_{PH} \sim 14$ Hz) for the P^1-methyls and doublets at δ_H 2.22 and 2.08 ($^2J_{PH} \sim 14$ Hz) for the P^2-methyls (assigned by means of $^1H-^{31}P\{^1H\}$ HSQC and NOE data). Likewise, the $^{13}C\{^1H\}$ spectrum reveals corresponding doublets at δ_C 6.3 ($^1J_{PC} \approx$

(17) Jennings, B. W. *Chem. Rev.* **1975**, *75*, 307.

Scheme 3[a]



[a] R = $(CH_2)_3OH$.

54 Hz) and 5.7 ($^1J_{PC} \approx 55$ Hz), and doublets at δ_C 5.0 ($^1J_{PC} \approx 53$ Hz) and 4.2 ($^1J_{PC} \approx 57$ Hz) (assigned by HSQC and HMBC data). For the Et_2PPh derivative **7g**, the CH_2 protons of each of the inequivalent Et groups at both P atoms are also anisochronous, and the experimental $^1H\{^{31}P\}$ spectrum is shown in Figure 6A. The simulated spectrum for the four CH_2 protons of the two sets of P^1-$(CH_2CH_3)_2$ atoms (two ABX_3 spin-systems), using (i) a shift difference of 0.228 ppm between the centers of the multiplets, (ii) shift differences of 0.145 and 0.110 ppm within each set of diastereotopic CH_2 protons, and (iii) the coupling constants $J_{AB} = 16.0$ Hz (geminal coupling) and $J_{AX} = J_{BX} = 7.7$ Hz (vicinal coupling), is shown in Figure 6B. Similarly, making the P^2-ethyl groups anisochronous by 0.442 ppm, the diastereotopic CH_2 protons anisochronous by 0.080 and 0.040 ppm, and using the above coupling constants, a $^1H\{^{31}P\}$ spectrum for the P^2-CH_2 protons can be simulated (Figure 6C). Superimposing the two simulated spectra (Figure 6D) mimics remarkably well the experimental spectrum (Figure 6A). The $^{13}C\{^1H\}$ shifts for the methylene carbons at P^1 and P^2 differ by 1.0 and 0.8 ppm, respectively, while the corresponding differences for the associated methyl carbons are 0.1 and 0.2 ppm.

In principle, similar anisochronous behavior at $P-CH_2$ centers must exist for all compounds of type **3**, **4**, **6**, and **7**, except for the PMe_3-containing species **(d** type). For example, for the Et_3P derivative **7a**, the anisochronous nature of the CH_2 protons at P^1 and P^2 is reflected in a ^1H NMR spectrum recorded in D_2O on a 600 MHz instrument. Instead of the "expected" overlapping doublet of quartets, a more complex multiplet pattern is seen, and this can be simulated as two overlapping ABX_3Y spin systems (Figure 7). The simulation uses at P^1, $\Delta\delta_{AB} = 0.069$ ppm, a geminal coupling constant $J_{AB} = 16.0$ Hz, vicinal coupling constants $J_{AX} = J_{BX} = 7.7$ Hz, and coupling with the phosphorus $J_{AY} = J_{BY} = 12.6$ Hz; at P^2, $\Delta\delta_{AB} = 0.043$ ppm, with the same coupling constants.

As noted earlier, **6a**−**g** and 7**a**−**g**, despite possessing two chiral centers, are each formed as an *R*,*R*/*S*,*S*-enantiomeric mixture. We have recently noted formation of just enantiomers in the aqueous reaction of cinnamaldehyde with $[HO(CH_2)_3]_3P$ in the presence of HCl (Scheme 3),[3] and it is likely that formation of all such bis(phosphonium) zwitterions or salts via a phosphine/α,β-unsaturated interaction will show analogous behavior.

Conclusions

Substituted cinnamaldehydes, used as lignin model compounds, react with $R_2R'P$ [R = R′ = Me, Et, $(CH_2)_3OH$; R = Me or Et, R′ = Ph] in water at ambient conditions under Ar to give a zwitterionic monophosphonium species. Generally, these then undergo self-condensation to form bis(zwitterionic) species; the phenolate oxygens of these can be protonated with HCl to give the corresponding bis(phosphonium) dichloride salts as a mixture of *R*,*R*- and *S*,*S*-enantiomers. ^{31}P ^1H, ^2D, and $^{13}C\{^1H\}$ NMR studies reveal that the mechanism involves initial nucleophilic attack of the phosphine at the C═C bond to form monophosphonium species that self-condense accompanied by phosphine migration; with the more bulky phosphines $^iPr_3P$, $MePPh_2$, $(cyclo\text{-}C_6H_{11})_3P$, and $Na[Ph_2P(m\text{-}SO_3\text{-}C_6H_4)]$, the self-condensation is not observed. The weakly nucleophilic $[NC(CH_2)_2]_3P$ does not react. Some exceptional ^1H NMR data recorded for the prochiral phosphorus centers of the bisphosphonium dichlorides are analyzed.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for funding via a Discovery grant and an Idea to Innovation (I2I) grant, and Drs. Nick Burlinson and Maria Ezhova for discussions about the NMR data.

Supporting Information Available: Crystallographic data (as CIF files) for compounds **7a** and **7d** and spectroscopic and analytical data for the compounds **6b** (α- and β-atropisomers), **6c**−**6g**, and **7c**−**7g (**Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

IC7007478