ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 5, pp. 840–847. © Pleiades Publishing, Ltd., 2012.
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Lignin-Type, α,β-Unsaturated Aldehydes of Lignin-Type in Organic Solvents

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Received March 22, 2011

Abstract—A 1:1 reaction of $[HO(CH_2)_3]_3P$ with 4-hydroxy-3-methoxy-cinnamaldehyde (coniferaldehyde) or 3,5-dimethoxy-4-hydroxycinnamaldehyde (sinapaldehyde) in acetone at room temperature affords phosphonium zwitterions of the type $R_3P^+CH(4\text{-}O^-\text{-}Ar)CH_2CHO$; other phosphines [R = Et, *n*-Bu, $(CH_2)_2CN$, and *p*-Tol] do not react under the same conditions. In alcohols R'OH(D) [R' = CD_3, Et, $(CD_3)_2CD$, *s*-Bu, $HOCH_2CH_2$], the above phosphines (except the cyano-derivative) and those where R = *i*-Pr, Cy, Me_2Ph, $MePh_2$ do react within an equilibrium established between the reactants and the zwitterion-hemiacetal products $R_3P^+CH(4\text{-}O^-\text{-}Ar)CH_2CH(OH)(OR')$ that are formed as a mixture of two diastereomers. The nature of the phosphine and the alcohol affects the equilibrium and the diastereomeric ratio.

DOI: 10.1134/S1070363212050064

Our group has been involved in investigating interactions of phosphines with unsaturated compounds in aqueous media, the interest evolving from discovery of the use of the water-soluble phosphine $(HOCH_2)_3P$ for the bleaching of pulps [1–4]. The topic is also of interest within homogeneous catalysis in aqueous media involving unsaturated organic substrates using transition metal-phosphine systems [5, 6]. A review covering both these aspects of the chemistry of this specific phosphine has appeared recently [7]. We have reported previously studies on the reactions of tertiary phosphines with substituted benzaldehydes [8], benzyl and cinnamyl alcohols [9], and quinones [10].

Prior to our detailed studies on the interaction of α,β-unsaturated aldehydes with tertiary phosphines in aqueous media [11, 12], these systems were not well understood, the relevant literature being summarized in our reports. The studies revealed that the reactions with aromatic α,β-unsaturated aldehydes depend on substituents present in the aromatic ring. Thus, cinnamaldehyde, in the presence of tris(hydroxypropyl)phosphine, $[HO(CH_2)_3]_3P$ (THPP), undergoes self-condensation into the two isomeric products shown in Scheme 1, the reaction being initiated by nucleophilic attack of the phosphine at the C-atom adjacent to the Ph group [11]; however, lignin-type aldehydes, which contain a *p*-OH-group, react with tertiary phosphines to afford bisphosphonium zwitterion products via the same nucleophilic phosphine attack (Scheme 2) [12].

Reactions of α,β-unsaturated aldehydes such as ArCH=CHCHO (Ar = aryl) with tertiary phosphines in organic media have been investigated recently, but only with (α-hydroxy)phosphines [e.g. $Ph_2PCH(OH)R$, where R = H, alkyl or aryl], which readily decompose reversibly to RCHO and Ph_2PH. The secondary phos-

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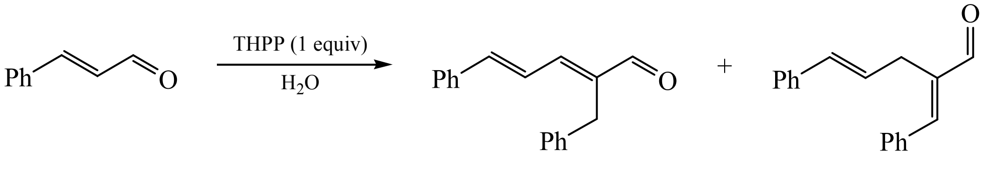
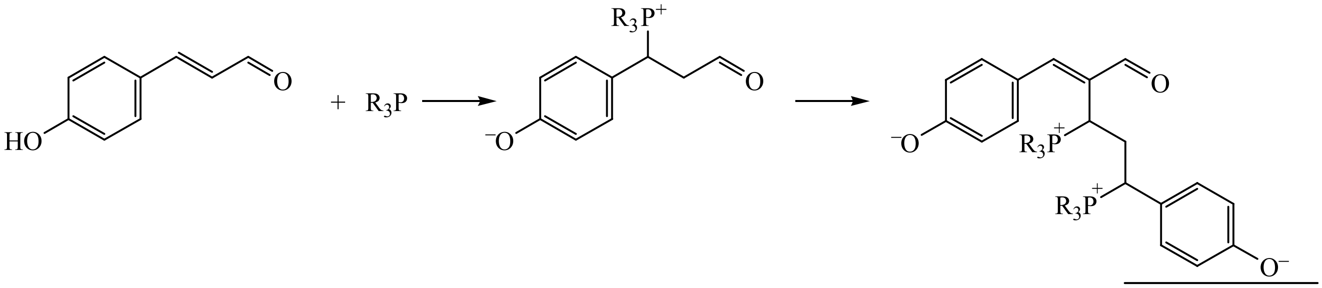
Scheme 1.



Scheme 2.

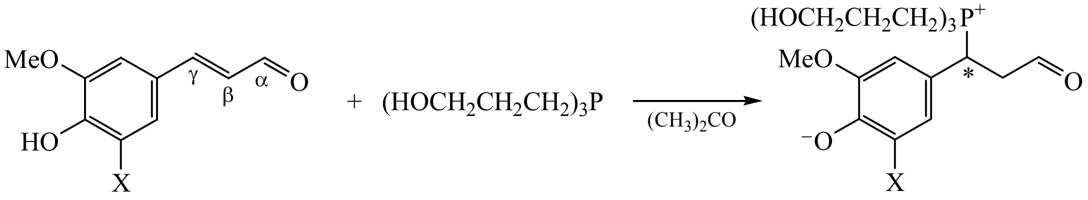


phine product adds across the olefinic bond to generate, in this exemplified case, $PPh_2C^*H(Ar)\cdot CH_2CHO$, where C* represents a chiral carbon center [13, 14]. Examples of enantioselective syntheses of this new type of tertiary phosphine have appeared, the products being more readily obtained by reactions of the unsaturated aldehydes with the secondary phosphines [14–16].

This current report describes results on the interaction of tertiary phosphines R_3P (R = Ar or alkyl) with lignin-type α,β-unsaturated aldehydes in acetone and in several alcohols.

A 1:1 reaction of THPP with coniferaldehyde (**Ia**) or sinapaldehyde (**Ib**) in acetone at room temperature under Ar gives immediate precipitation, respectively, of a yellow or yellow-brownish phosphonium zwitterion (**IIa** or **IIb**) as a mixture of (*R*)- and (*S*)-stereoisomers (Scheme 3) that are the products of γ-nucleophilic attack by the phosphine. The products **IIa** and **IIb**, which are formed in high yield, are insoluble in acetone, CH_2Cl_2, $CHCl_3$, and CH_3CN, but are readily soluble in water, MeOH, and DMSO.

Scheme 3.

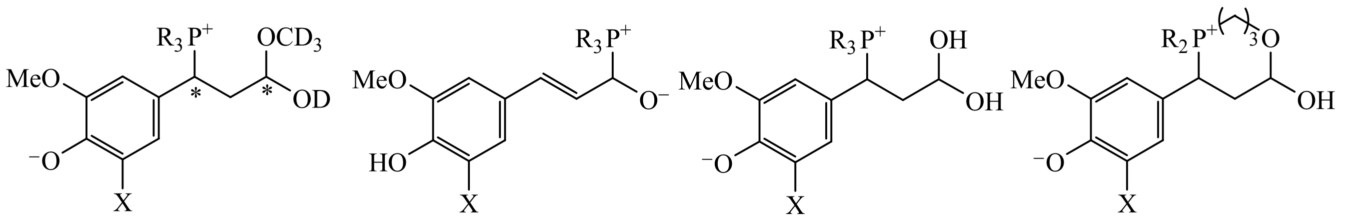


X = H (**Ia**), MeO (**Ib**)

X = H (**IIa**), MeO (**IIb**).

Dissolution of **IIa** or **IIb** in CD_3OD gives a red solution in which there is ~70% conversion to the corresponding hemiacetal of the phosphonium salts (**IIIa** or **IIIb**, respectively) while the remaining 30% reconverts to THPP and **Ia** (or **Ib**). The $^{31}P-\{^1H\}$ and ^1H NMR signals of THPP are seen; as well as the corresponding ^1H signals of **Ia** or **Ib**, implying reversible equilibria as shown in the top half of Scheme 4, the aldehydes **Ia** and **Ib** in CH_3OH/CD_3OD do not form hemiacetals as evidenced by ^1H NMR spectroscopy.

Scheme 4.

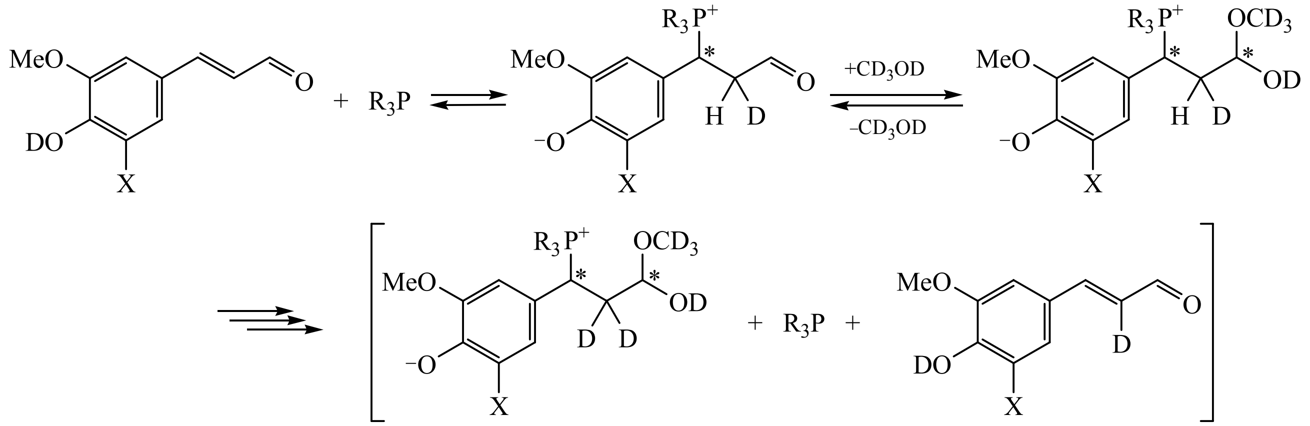


IV

Va, Vb

VI

X = H (**IIIa**), MeO (**IIIb**), R = $(CH_2)_3OH$.



Species **IIIa** and **IIIb** are each present as a mixture of two diastereomers, and the NMR data for both systems are essentially the same; data for just the **IIa** system are presented here. The ^{31}P–{^{1}H} spectrum reveals the **IIIa** diastereomers as two, slightly different in intensity singlets in the phosphonium region [12] at δ_P 37.8 and 37.4 ppm (cf. Table 1, entry 3). The reversibility (see Scheme 4) is confirmed by observed slow H/D-exchange processes, monitored by ^{1}H NMR spectroscopy. Fifteen minutes after dissolution of **IIa**, the α-proton of each **IIIa** diastereomer appears as a triplet of doublets (at δ_H 4.47 and 4.44 ppm, respectively) due to coupling to the two β-protons ($^3J_{HH}$ 4.0 Hz) and to the P-atom ($^4J_{PH}$ 0.8 Hz); the β-protons appear, respectively, as broad multiplets at δ_H 2.44 and 2.04 ppm, while the γ-proton signal (at δ_H ~3.84 for both diastereomers) overlaps with the OMe resonances, and the *J* values cannot be determined. After 24 h, the β-proton signals have disappeared, and the corresponding α-proton triplets of doublets have simplified to doublets ($^4J_{PH}$ 0.8 Hz) implying replacement of both β-protons by deuterons; simultaneously, the β-proton signal of **Ia** (δ_H 6.53 ppm, d.d) disappears and the α- and γ-protons resonances collapse into singlets at δ_H 9.44 and 7.53 ppm, respectively. That two β-protons were initially detected for **IIIa** is consistent with **IIa** being the synthesized, solid product in acetone. If the product resulted from nucleophilic phosphine attack at the α-carbon (exemplified by **IV**), then its dissolution in CD$_3$OD, following typical rapid decomposition of the α-(hydroxy)phosphonium zwitterion to give free phosphine

Table 1. ^{31}P–{^{1}H} and selected ^{1}H NMR data, and equilibrium data for a phosphine and its phosphonium hemiacetal product formed in a 1:1 reaction with sinapaldehyde (**Ib**) in CD$_3$OD at room temperature under Ar

Entry	Phosphine	R$_3$P, δ_P	(*RS*)/(*SR*)[a]			(*RR*)/(*SS*)[a]			R'R$_3$P$^+$/R$_3$P	*dr*[b]
			δ_P	α-H, δ_H	γ-H, δ_H	δ_P	α-H, δ_H	γ-H, δ_H		
1	Et$_3$P	–17.5	40.1	4.37	3.74	39.7	4.33	3.73	5.2	1.1
2	*n*-Bu$_3$P	–30.5	35.4	4.38	3.74	35.0	4.33	3.72	4.0	1.1
3	THPP	–29.5	37.8	4.36	[c]	37.4	4.32	[c]	2.5	1.1
4	Me$_2$PPh	–45.5	27.9	4.32	3.92	27.6	4.28	3.90	2.5	1.1
5	MePPh$_2$	–26.7	26.4	4.37	4.66	26.1	4.31	4.65	0.4	1.2
6	*i*-Pr$_3$P	20.8	41.6	4.28	4.04	41.2	4.20	4.01	0.7	1.2
7	Cy$_3$P	12.3	32.9	4.29	[c]	32.5	4.21	[c]	[d]	1.2
8	[NC(CH$_2$)$_2$]$_3$P[e]	–22.5	–	–	–	–	–	–	–	–

[a] The assignments of the diastereomers are tentative (see text). [b] *dr* = diastereomeric ratio. [c] Overlap with OMe resonances. [d] See text. [e] No reaction with this phosphine.

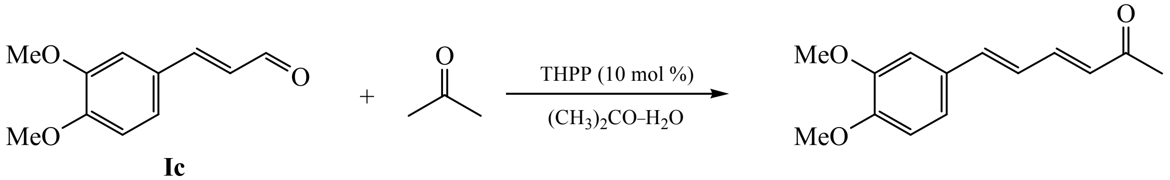
and unsaturated aldehyde (see Scheme 3 in [11]), would generate a monodeuterated hemiacetal via THPP attack at the γ-C atom (Scheme 4, top half), and the two β-protons would not be observed. When a 10-fold excess of **Ia** was added under Ar to the NMR tube containing **IIa** in CD_3OD, the $^{31}P-\{^1H\}$ and ^1H NMR resonances of THPP disappeared as the equilibria are pushed to the right (Scheme 4) and only **IIIa** and **Ia** were detected, the β-proton of the latter again being slowly replaced by deuteron.

Dissolution of **IIa** and **IIb** in D_2O revealed chemistry that we have reported previously [12]. The initial $^{31}P-\{^1H\}$ solution spectrum of **IIb** revealed singlets at δ_P 37.9 and 37.1 ppm in a 1:12 ratio corresponding, respectively, to **IIb** and its diol **Vb**, both previously characterized (species 3e and 4e in [12]). The $^{31}P-\{^1H\}$ spectrum of **IIa** correspondingly shows 1:9 intensity singlets at δ_P 38.0 and 37.2 ppm for **IIa** and **Va**, respectively. The ^1H spectra also prove the formation of the phosphonium salts (**IIa**, **IIb**, and their respective diols **Va** and **Vb**); the data for **IIb** and **Vb** are as reported earlier [12], while the data for the α-, β-, γ-proton moieties of **IIa** and **Va** are essentially the same. Parallel ^1H NMR data have been discussed for the corresponding reactions of sinapaldehyde (**Ib**) with Et_3P and *i*-Pr_3P [12]. The **IIa** and **IIb** systems subsequently undergo slow self-condensation to generate bisphosphonium zwitterionic species, chemistry that again has been well substantiated [12]. The low-resolution ESI-MS of **IIa** (or **IIb)** freshly dissolved in H_2O shows peaks at *m/z* 387.3 and 405.3 (or *m/z* 417.3, 435.3) that correspond to the protonated forms of **IIa**, **Va** and **IIb**, **Vb**, respectively. Dissolution of **IIa** or **IIb** in DMSO-d_6 solution generated green solutions whose NMR spectra showed decomposition back to the precursor aldehyde and THPP. The origin of the green color is unknown, but must result from a species formed by a weak, non-NMR detectable interaction (presumably acid-base or H-bond) between THPP (likely an OH group [7]) and the carbonyl- or phenol-oxygen of the aldehyde.

Treatment of 3,4-dimethoxy-cinnamaldehyde (**Ic**) with THPP under the same conditions (acetone, room temperature, Ar) does not form a type-**II** phosphonium zwitterion, confirming an already well-established, obvious point [8, 12] that the presence of a *p*-OH-group is critical for generation of the $O^-\cdots P^+$ zwitterions. Of note, when coniferaldehyde **Ia** was reacted with Et_3P, *n*-Bu_3P, $[NC(CH_2)_2]_3P$ or *p*-Tol_3P at a 1:1 ratio in acetone under Ar, no precipitation was observed and the $^{31}P-\{^1H\}$ spectra revealed just the signal of the free phosphine; however, when the Et_3P system was monitored in acetone-d_6 containing trace water, slow H/D exchange of the aldehyde β-proton was observed, implying the presence of a reversible reaction that lies on the side of the reactants. It seems that the insolubility of **IIa** and **IIb** in acetone allows for their complete formation, the corresponding equilibria being forced to the right-hand side. Not completely ruled out is the possibility that a hydroxylpropyl group of THPP forms a hemiacetal such as **VI** via an intramolecular interaction within **IIa, IIb**. The solution NMR and MS data could be consistent with the hemiacetal formulation, and spectroscopic evidence has been presented for such a 6-membered ring species formed from reaction of coniferaldehyde and $(CH_2OH)_3P$ in aqueous dioxane [4], but the formation of an 8-membered ring species such as **VI** seems highly unlikely.

A difference between **Ia** and **Ic** is also seen with the use of a catalytic amount of THPP (6–10%). In an acetone-d_6/D_2O mixture (1:1 by volume, room temperature, Ar), a slow H/D-exchange of the β-proton of **Ia** takes place. After 3 days, the intensity of the β-proton NMR signal (d.d, δ_H 6.57 ppm) has decreased by 75%; a $^{31}P-\{^1H\}$ singlet at δ_P 38.2 ppm attributable to **Va** was detected, and a set of low intensity ^1H resonances due to the THPP moiety of **Va** was also observed (see [12]). When **Ic** was used with the catalytic amount of THPP at room temperature in acetone–H_2O (1:1 by volume, room temperature, Ar), the cross-condensation product 6-(3,4-dimethoxyphenyl)-3,5-hexadien-2-one was isolated (Scheme 5). The corresponding reaction with cinnamaldehyde was described in our previous paper, where this THPP-promoted classic base-catalyzed aldol-type condensation was discussed in detail [11].

Scheme 5.



As discussed above, in CD_3OD solution an equilibrium exists between the free phosphine and unsaturated aldehyde reactants and the phosphonium hemiacetal products (Scheme 4). The effect of the nature of the phosphine in reaction with sinapaldehyde **Ib** (at room temperature, under Ar) was studied, and the data, measured after 24 h when the H/D exchange processes are complete, are summarized in Table 1. The $^{31}P-\{^1H\}$ and ^1H NMR data are closely analogous to those discussed above in detail for the THPP/coniferaldehyde (**Ia**) system. The specific diastereomer assignments of the $^{31}P-\{^1H\}$ signals are tentative, and are based on our earlier studies on reactions of cinnamaldehyde with tertiary phosphines in aqueous media [11], and on neat reagent reactions of cinnamaldehyde with Ph_2PH [14]: such reactions are stereospecific and in the diastereomeric products the (*RR*)/(*SS*) product was favoured over the (*RS*)/(*SR*) product. Thus, for the diastereomeric mixture of phosphonium-hemiacetals, the most intense $^{31}P-\{^1H\}$ signal (see Fig. 1) is assigned to the (*RR*)/(*SS*) product. In all the systems, the α-H of the (*RS*)/(*SR*) and (*RR*)/(*SS*) isomers appears in the ^1H spectrum as a doublet in the range δ_H 4.28–4.38 and 4.20-4.33 ppm, respectively (Table 1), due to weak coupling to the P-atom ($^4J_{PH} \approx$ 1 Hz); the corresponding γ-H appears as a doublet in the range δ_H 3.74–4.66 and 3.72–4.65 ppm, respectively ($^2J_{PH} \approx 15.5$ Hz), although in the THPP system the δ_H shift for the γ-H cannot be determined due to overlap with the OMe resonances. The data suggest that the $R'R_3P^+/R_3P$ product ratio, where R' represents the phenolate form of the sinapaldehyde moiety, depends on both steric and electronic factors of the phosphine. The highest value of 5.2 (Entry 1 and Fig. 1b) is seen with Et_3P, which has a cone angle θ of 132° [17], while *n*-Bu_3P and $[NC(CH_2)_2]_3P$ with the same θ value have ratio values of 4.0 and zero, respectively (entries 2 and 8); the trend of Et_3P > *n*-Bu_3P > the non-reactive $[NC(CH_2)_2]_3P$ likely corresponds to decreasing nucleophilicity of the phosphine, although the nuclophilicities of Et_3P and *n*-Bu_3P are essentially the same [18]. The THPP data (entry 3) with a ratio value of 2.5 fit this trend if the reasonable assumptions are made that θ for THPP is also 132°, and that its nucleophilicity lies between that of $[NC(CH_2)_2]_3P$ and *n*-Bu_3P. Me_2PPh, with the lowest θ (122°) gives a ratio of 2.5, while the low ratio value of 0.4 for $MePPh_2$ (θ = 136°) must be due to the negative effect of Ph groups on the nucleophilicity (Entries 4 and 5). The bulkier phosphine *i*-Pr_3P (θ = 160°) gives a product ratio of 0.7 (Entry 6), while the ratio for the most bulky tricyclohexylphosphine, Cy_3P (θ = 170°), was immeasurable because of the low solubility of Cy_3P in CD_3OD. The product diastereotopic ratio is

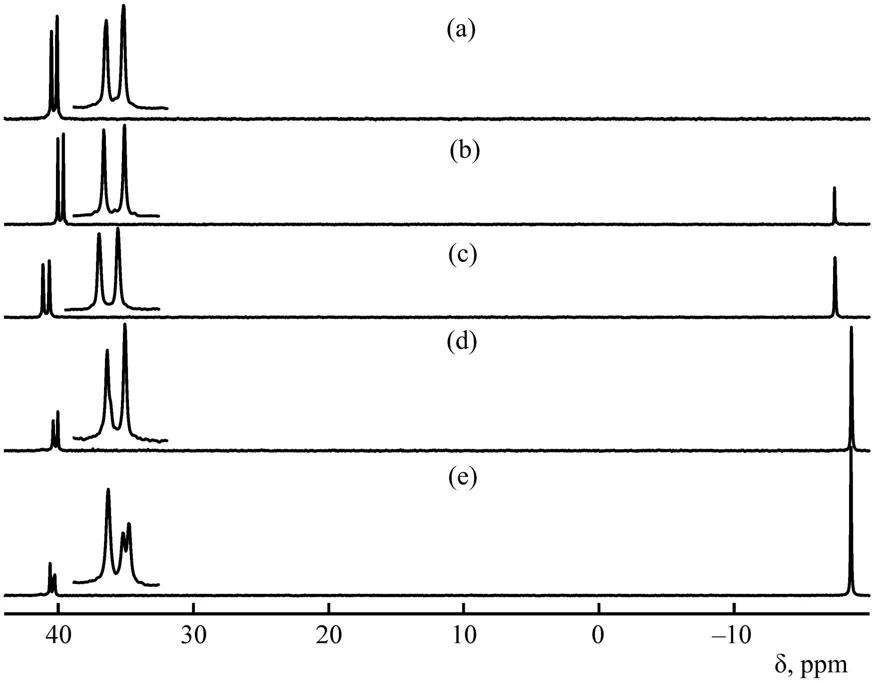


Fig. 1. $^{31}P-\{^1H\}$ spectrum of a solution of Et_3P and **Ib** (1:1, Ar) in: (a) $(CH_2OH)_2$, (b) CD_3OD, (c) EtOH, (d) *i*-PrOD-d_8, and (e) *s*-BuOH.

Table 2. $^{31}P-\{^1H\}$ NMR data and equilibrium data for Et_3P and its phosphonium hemiacetal product formed from **Ib** in different alcohols (1:1 reaction, room temperature, Ar)

Entry	Solvent	ε	R_3P, δ_P	(*RS*)/(*SR*), δ_P	(*RR*)/(*SS*), δ_P	$R'R_3P^+/R_3P$	*dr*
1	$(CH_2OH)_2$	37.7	–	40.4	40.0	∞	1.2
2	CD_3OD	32.7	–17.5	40.1	39.7	5.2	1.1
3	EtOH	24.6	–17.5	41.1	40.7	1.7	1.1
4	*i*-PrOD-d_8	18.3	–18.8	40.4	40.0	0.5	1.3
5	*s*-BuOH	15.8	–18.7	[a]	[a]	0.4	[a]
6	*t*-BuOH[b]	12.5	–18.9	–	–	0	–

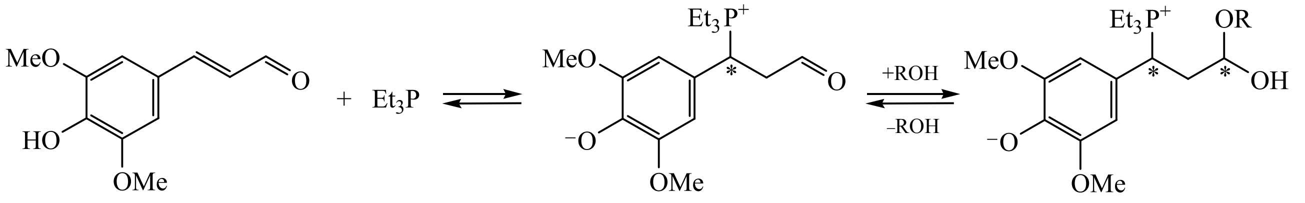
[a] See the text. [b] No reaction.

close to unity and varies little within the systems, with the bulkier $MePPh_2$, *i*-Pr_3P and Cy_3P affording the highest diastereotopic ratio value of 1.2.

The effect of using different alcohols for the 1:1 Et_3P/**Ib** reaction was also studied under the room temperature/Ar conditions, and Table 2 shows the equilibria data measured after 24 h (see Scheme 6, where within the CD_3OD and *i*-PrOD-d_8 systems the OH and β-H atoms will be present as D-atoms). The data strongly suggest that the $R'R_3P^+/R_3P$ product ratio depends on the dielectric constant (ε) of the alcohol. In glycol, with the highest ε value (37.7), quantitative yield of the phosphonium hemiacetal is seen (entry 1 and Fig. 1a). Within other alcohols, the intensity of the $^{31}P-\{^1H\}$ signal of Et_3P gradually increases (i.e. the equilibria shift to the left) in the order: CD_3OD (ε = 32.7) > EtOH (24.6) > $(CD_3)_2CDOD$ (18.3) > *s*-BuOH (15.8), as shown in Fig. 1. The zwitterionic product is clearly stabilized in a higher dielectric medium. Marginally greater variation in the diastereotopic ratio values is seen when the alcohols are varied, the *i*-PrOD-d_8 system having the highest value of 1.3 (but see below).

In the case of *t*-BuOH (ε = 12.5), which has a melting point of 25°C, the solubility of **Ib** is low, and so the reaction mixture (initially of a green color) was warmed until the aldehyde had dissolved to give a brown solution; however, no phosphonium $^{31}P-\{^1H\}$ signal was seen, and after 2 h at room temperature, when the solution again became green, still no phosphonium resonances were detected. Of note, the reaction mixture in *s*-BuOH (see below) is deep red, while in glycol the color is orange. The reasons for the observed varying colors are unclear: interaction of the alcohols with the reactant aldehyde (see the DMSO system above where no zwitterionic product is seen), or with the phenolate-oxygen of the phosphonium hemiacetal, might be involved.

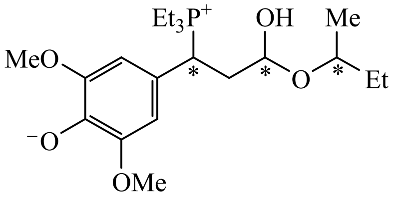
Scheme 6.



VII

A 1:1 reaction of Et_3P with 4-methoxy-cinnamaldehyde in CD_3OD after 25 min reveals a broad singlet in the phosphonium region at δ_P 40.5 in the $^{31}P-\{^1H\}$ spectrum, and this is attributed to a cationic phosphonium species; however, the system is unstable, and new $^{31}P-\{^1H\}$ resonances are generated over one day. The system shows similarities to the reaction of cinnamaldehyde with THPP in water (or D_2O), which finally generates two isomeric self-condensation aldehyde products with co-production of the phosphine oxide (Scheme 1) [11]. Kinetic and mechanistic details have recently been published by Galkin's group on the related but simpler reactions of α,β-unsaturated carboxylic acids with Ph_3P where, for example, acrylic acid in acetic acid media gives just the phosphonium acetate $[Ph_3P^+CH_2CH_2CO_2H]OAc^-$ [19], while in alcohol media the $Ph_3P^+CH_2CH_2CO_2^-$ zwitterion is formed [20].

In the case of the chiral alcohol *s*-BuOH, the stereochemistry is necessarily more complicated. Four $^{31}P-\{^1H\}$ phosphonium resonances were anticipated due to the four possible diastereomers, (*SSS*)/(*RRR*), (*SSR*)/(*SRR*), (*SRS*)/(*RSR*), and (*RSS*)/(*RRS*) (see **VIII**), but only three singlets at δ_P 40.4, 40.1 and 40.0 ppm with relative intensity 1.0:0.5:0.6 were detected (Fig. 1e). One rational is that the chirality at the γ-C atom of **VII** (see Scheme 6) determines the chirality of an attacking molecule of *s*-BuOH. For example, if the γ-C atom has (*S*)-chirality perhaps only (*S*)-butanol can lead to the hemiacetal and vice versa; in this case only two diastereomers are possible [(*SSS*)/(*RRR*) and (*SRS*)/(*RSR*)]. Further, if the hemiacetal formation is not complete in this solvent, one of the three resonances could be that of **VII**. Of note in this regard, the minor resonance in the $^{31}P-\{^1H\}$ spectrum of the reaction mixture in *i*-PrOD-d_8 (Fig. 1d) does show a shoulder that could be due to free **VII** and, in which case, the actual diastereotopic ratio would be higher than 1.3.



VIII

CONCLUSIONS

The interactions of tertiary phosphines with lignin-type α,β-unsaturated aldehydes in organic media (Schemes 3 and 4) are different from those studied previously in aqueous solution. The solvent, the phosphine, and the aldehyde all affect the nature of the products. In acetone, only $[HO(CH_2)_3]_3P$ of the phosphines studied reacts with coniferaldehyde (**Ia**) or sinapaldehyde (**Ib**) to precipitate the phosphonium zwitterions $[HO(CH_2)_3]_3P^+CH(4\text{-}O^-\text{-}Ar)CH_2CHO$; Et_3P, *n*-Bu_3P, $(NCCH_2CH_2)_3P$, and *p*-Tol_3P were unreactive. Aldehydes without a *p*-OH group do not react with $[HO(CH_2)_3]_3P$. **Ia** and **Ib** react with tertiary phosphines in MeOH via an equilibrium process to give the corresponding phosphonium hemiacetals, $R_3P^+C^*H(4\text{-}O^-\text{–}Ar)CH_2C^*H(OH)(OMe)$, in a diastereomeric ratio of 1.1–1.2. Stronger donor phosphines shift the equilibrium to the product side, while the bulkier phosphines give the diastereotopic ratio value of 1.2. Alcohols with higher dielectric constant favor significantly the formation of the zwitterionic hemiacetals, while a bulky alcohol increased the product diastereotopic ratio. In DMSO, the equilibrium reaction with THPP lies completely to the left.

EXPERIMENTAL

Sinapaldehyde, coniferaldehyde, and other aldehydes were used as received from Aldrich. 4-Methoxy-cinnamaldehyde and 3,4-dimethoxy-cinnamaldehyde were prepared by condensing acetaldehyde with 4-methoxybenzaldehyde and 3,4-dimethoxybenzaldehyde, respectively [21]. THPP (an oil, > 80%), *n*-Bu_3P, Et_3P, Me_2PPh, $MePPh_2$, Cy_3P, *i*-Pr_3P (all Strem products) and *p*-Tol_3P (Aldrich) were used without purification, while $[NC(CH_2)_2]_3P$ was prepared by a literature method [22]. D_2O, CD_3OD, DMSO-d_6, acetone-d_6, and *i*-PrOD-d_8 (Cambridge Isotope Labs.) were used as received. Acetone was dried over $CaCl_2$, distilled under N_2, degassed by a freeze-pump-thaw technique, and then saturated with Ar. Ethylene glycol was stirred for 2 days under Ar at 50°C and then distilled under vacuum; *s*-BuOH was refluxed under Ar for 4 h and then distilled; EtOH was dried over CaH_2 and then distilled under Ar. NMR spectra were recorded on a Bruker AV300 spectrometer at 300 K (300 MHz for ^1H; 121 MHz for $^{31}P-\{^1H\}$), with a residual deuterated solvent proton (relative to external $SiMe_4$) and 85% aq. H_3PO_4 being used as references; s = singlet, d = doublet, t = triplet, m = multiplet; *J* values are given in Hz. Elemental analyses were performed on a Carlo Erba 1108 analyzer. Low resolution mass spectrometry was performed on a Bruker Esquire electrospray (ESI) ion-trap spectrometer with samples dissolved in H_2O; the positive ion polarity scanned the range 60-1000 *m/z*.

Synthesis of IIa from THPP and coniferaldehyde (Ia). A solution of THPP (100 mg, 0.48 mmol, assuming 100% purity) in acetone (1.5 ml) was added to a solution of **Ia** (86 mg, 0.48 mmol) in acetone (1.5 ml), and the mixture was stirred for 3 h at r.t. (~20°C) under Ar. The yellow solid product was filtered off, and dried under vacuum overnight (yield 145 mg, 78%). $C_{19}H_{31}O_6P$. Calculated, %: C 59.06, H 8.09. Found, %: C 59.3, H 8.4. Low-resolution ESI-MS: *m/z*

387.3 (80%) $[M + H]^+$, 405.3 (100%) $[M + H_2O + H]^+$; M_{calc} 386.4. ^1H and $^{31}P–\{^1H\}$ NMR data (and for **IIb** see below) are discussed in the Results and Discussion section.

Synthesis of IIb from THPP and sinapaldehyde (Ib). Use of the procedure given above, but with **Ib** (100 mg, 0.48 mmol), produced a yellow-brown solid (yield 140 mg, 70%). $C_{20}H_{33}O_7P$. Calculated, %: C 57.68, H 7.99. Found, %: C 57.3, H 8.1. Low-resolution ESI-MS: *m/z* 417.3 (40%) $[M + H]^+$, 435.3 (100%) $[M + H_2O + H]^+$; M_{calc} 416.4.

NMR study of coniferaldehyde/THPP (16:1) reaction in acetone-d_6/D_2O. A solution of THPP (2.1 mg, 0.01 mmol) in D_2O (1 ml) was added to a solution of coniferaldehyde (28.5 mg, 0.16 mmol) in acetone-d_6 (1 ml) under Ar at r.t. The mixture was stirred for 5 min, when 0.7 ml of the solution was transferred into a J-Young NMR tube under Ar; the NMR spectra were then recorded periodically (see Results and Discussion).

Aldol condensation of 3,4-dimethoxy-cinnamaldehyde and acetone in the presence of THPP. A 2 ml, air-free aqueous solution of THPP (21 mg, 0.1 mmol) was added to a 2 ml air-free acetone solution of the aldehyde (192 mg, 1.0 mmol), and the mixture was stirred under Ar for 20 h at r.t. Removal of the solvents left a brown solid that was extracted with Et_2O (2×5 ml); the ether layers were dried with Na_2SO_4 overnight, and the product was separated by column chromatography on silica gel (230–400 mesh) using Et_2O as eluent. Removal of Et_2O in vacuo gave 6-(3,4-dimethoxyphenyl)-3,5-hexadien-2-one as a yellow solid (yield 153 mg, 66%). ^1H NMR spectrum ($CDCl_3$), δ_H, ppm: 7.28 d.d (1H, C*H*=CHCO, $^3J_{HH}$ 15.5, $^3J_{HH}$ 15.5 Hz), 7.06–6.99 m (2H, *m*- and *o-H*), 6.93–6.70 m (3H, ArC*H*=C*H* and *o-H*), 6.23 d (1H, CH=C*H*CO, $^3J_{HH}$ 15.4 Hz), 3.93 s (3H, OCH_3), 3.91 s (3H, OCH_3), 2.31 s (3H, CH_3).

NMR study of the 1:1 reaction of sinapaldehyde (Ib) with phosphines in alcohols. A phosphine (0.15 mmol; 22 μl Et_3P, 37 μl *n*-Bu_3P, 29 μl *i*-Pr_3P, 21 μl Me_2PPh, 28 μl $MePPh_2$, 31.0 mg THPP) was added to a solution of **Ib** (31.0 mg, 0.15 mmol) in an alcohol (1 g) under Ar; 0.7 ml of the solution was transferred into a J-Young NMR tube under Ar, and the $^{31}P–\{^1H\}$ NMR spectra were recorded periodically (see Results and Discussion). Different concentrations of Cy_3P and $[NC(CH_2)_2]_3P$ were used because of their low solubility: 13.5 mg (0.05 mmol) Cy_3P and 10.0 mg (0.05 mmol) aldehyde; $[NC(CH_2)_2]_3P$ 13.9 mg (0.07 mmol) and 15.0 mg (0.07 mmol) aldehyde.

ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council of Canada for funding via a Discovery Grant.

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