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Interaction of PH_3 with Acetaldehyde in Aqueous Media and Chemistry of $[HO(Me)CH]_4PCl$

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Abstract—The known phosphonium chloride $[HO(Me)CH]_4PCl$ was prepared at ambient conditions from PH_3 and acetaldehyde in aqueous HCl, and characterized by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Attempts to obtain the tertiary phosphine $[HO(Me)CH]_3P$ via reaction of $[HO(Me)CH]_4PCl$ with Na_2SO_3 or Et_3N in aqueous media under Ar revealed that $[HO(Me)CH]_3P$ is unstable and equilibrates with the secondary phosphine $[HO(Me)CH]_2PH$ and acetaldehyde. A 1:4 reaction of $[HO(Me)CH]_4PCl$ with $NaHSO_3$ at room temperature under Ar affords first the oxide $[HO(Me)CH]_2P(O)H$ and then the phosphinic acid $[HO(Me)CH]_2P(O)OH$. A 1:1 reaction of $[HO(Me)CH]_4PCl$ with $Na_2S_2O_3$ affords the sulfide $[HO(Me)CH]_3PS$. $^{31}P\{^1H\}$ and ^1H NMR data for all the (α-hydroxyethyl)phosphorus species are reported for the first time.

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(α-Hydroxymethyl)phosphines and the corresponding phosphonium salts have attracted much attention, and this is exemplified by a recent review on the diverse coordination chemistry of $(HOCH_2)_3P$ and its industrial applications [1]. This phosphine, readily formed from the phosphonium salt $(HOCH_2)_4PCl$ (or the corresponding sulfate) has been used commercially as a bleaching and brightness stabilizing agent of mechanical pulps [2–6], and as a component for flame- and glow-resistant polymers [7–9]. There is also a patent on use of the oxide and sulfide derivatives, $(HOCH_2)_3PO$ and $(HOCH_2)_3PS$, in the manufacture of fire-retardant polyurethanes [10]. The $(HOCH_2)_4PCl$ salt can be obtained by passing PH_3 through a solution of formaldehyde in the presence of HCl, a carbonyl-hydrophosphination reaction [11–14], and treatment of this salt with a base such as NaOH [15, 16], Et_3N [17, 18], or Bu_3P [19], or interaction with Na_2SO_3 [8, 20], affords $(HOCH_2)_3P$, which is stable (even under air) in aqueous media at pH 7.0–8.0 [21].

Reports on syntheses of other tetrakis(α-hydroxyalkyl)phosphonium chlorides are few, although tetrakis-(α-hydroxyethyl)phosphonium chloride, $[HO(Me)CH]_4 \cdot PCl$ (**I**), and the α-hydroxypropyl analogue $[HO(Et)\cdot CH]_4PCl$ were apparently prepared in 1888 via hydrophosphination reactions of PH_3 with acetaldehyde and propionaldehyde, respectively, in the presence of HCl [22]. The chloride **I** and the $[HO(R)CH]_4PCl$ analogues (R = n-C_6H_{13} and n-$C_{11}H_{23}$) were similarly prepared in the early 1960s, but characterized only by elemental analysis and/or melting point [13]. In 1998, $[HO(R)CH]_4PCl$ (R = n-C_9H_{19} and again n-$C_{11}H_{23}$) were synthesized by the same methodology, and their characterization now included ^1H-, $^{31}P\{^1H\}$-, and $^{13}C\{^1H\}$-NMR data [23]. Reaction of aldehydes, branched at the α-position, with PH_3/HCl affords only secondary (α-hydroxyalkyl)phosphine derivatives [13]. To the best of our knowledge, the only reported example of a tertiary tris(α-hydroxyalkyl)phosphine other than $(HOCH_2)_3P$ is $[HO(Cl_3C)CH]_3P$ [24].

Following the discovery of the pulp-bleaching activity of $(HOCH_2)_3P$, a strong reductant and nucleophile [1–6], our group has investigated interactions of tertiary or secondary phosphines with substituted benzaldehydes [25], benzyl and cinnamyl alcohols [26], quinones [27], and α,β-unsaturated aldehydes [28–32]. The general conclusion is that the bleaching activity occurs by the loss of conjugation in organic frameworks. A general problem associated with the use of $(HOCH_2)_3P$, and (α-hydroxyalkyl)phosphines, is

$$PH_3 \overset{RCHO}{\rightleftharpoons} [HO(R)CH]PH_2 \overset{RCHO}{\rightleftharpoons} [HO(R)CH]_2PH \overset{RCHO}{\rightleftharpoons} [HO(R)CH]_3P \overset{\substack{RCHO \\ HCl}}{\rightleftharpoons} [HO(R)CH]_4PCl \qquad (1)$$

the reversibility of their formation via phosphine/aldehyde reactions as shown in Eq. (1) [21, 25, 28, 30, 31], and this led us to study the preparation, stability, and chemical properties of tris(α-hydroxyethyl) phosphine, $[HO(Me)CH]_3P$ (**II**).

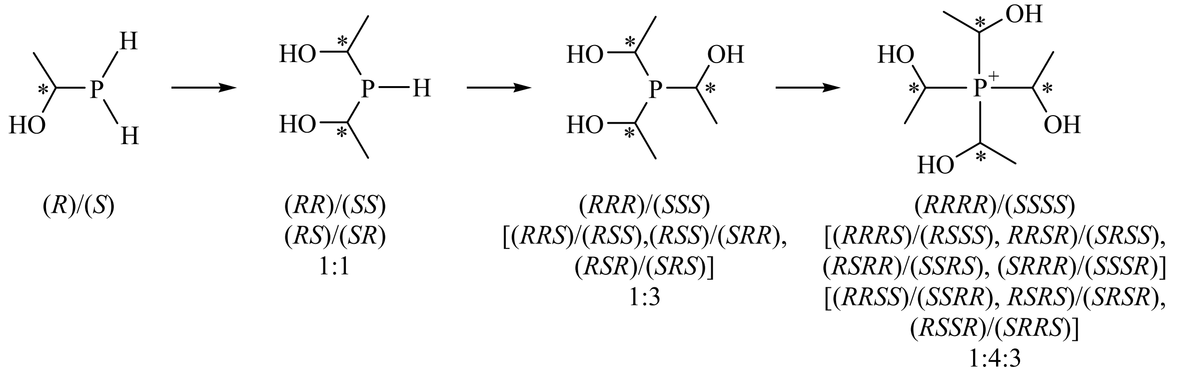
This report describes NMR data for **I** and its reactions with Et_3N and Na_2SO_3 in attempts to obtain the tertiary phosphine **II**. Interactions of **I** with $NaHSO_3$ and $Na_2S_2O_3$, sulfur-containing salts that are decomposition products of sodium dithionite ($Na_2S_2O_4$), are also described, the interest here being associated with the synergic effect observed for a combination of $(HOCH_2)_3P$ and dithionite in pulp-bleaching [33, 34].

Pure chloride **I** was prepared by a PH_3/acetaldehyde/HCl reaction in water, with a final recrystallization of the isolated residue from EtOH; a literature method used an aqueous/THF solvent and, for the residue, a trituration procedure with MeCN [13]. The product is highly water-soluble and its solution is stable in air, as is $(HOCH_2)_4PCl$ [21]. The $^{31}P\{^1H\}$ spectrum in D_2O revealed three singlet resonances: a smaller one at δ_P 27.6 ppm and two of equal intensity at δ_P 28.3 and 27.8 ppm, the integration ratios being 1:4:4. These ratios remain constant in all the chloride **I** reactions studied, implying that the three resonances are associated with the phosphonium chloride [more correctly **I**-d_4, as defined in Eq. (2)] containing four identical, chiral C-centers bonded to a tetrahedral P-atom. Theoretically, three $^{31}P–\{^1H\}$ resonances corresponding to three possible diastereomers should be observed in a 1:4:3 ratio: one (*RRRR*)/(*SSSS*) isomer, four isomers of identical structures where only one group is different [(*RRRS*)/(*RSSS*) = (*RRSR*)/(*SRSS*) = (*RSRR*)/(*SSRS*) = (*SRRR*)/(*SSSR*)], and three isomers with structures where two groups are different [(*RRSS*)/(*SSRR*) = (*RSRS*)/(*SRSR*) = (*RSSR*)/(*SRRS*)] (see Scheme 1). The smaller 27.6 ppm signal is thus attributed to the (*RRRR*)/(*SSSS*) diastereomer. The slight deviation from the expected ratio possibly results from an equilibrium present in D_2O (Eq. 2), similar to the one established for $(HOCH_2)_4PCl$ (pK_d ~ 7.1 [21, 35, 36]); this equilibrium might favor one of three **I**-d_4 diastereomers, because of steric hindrance caused by the deuteroxyethyl groups within $[DO(Me)CH]_3P$ (**II**-d_3). For the phosphonium salts $[HO(n\text{-}C_9H_{19})CH]_4PCl$ and $[HO(n\text{-}C_{11}H_{23})CH]_4PCl$, three δ_P resonances were detected in ratios of 2:3:5 and ~1:2:3, respectively, and were reported as 'nearly identical' to the statistical value [23].

$$\underset{\mathbf{I}\text{-}d_4}{[DO(Me)CH]_4P^+Cl} \xrightarrow{K_d} \underset{\mathbf{II}\text{-}d_3}{[DO(Me)CH]_3P} + MeCHO + DCl \qquad (2)$$

The CH_3 protons of the chloride **I**-d_4 are seen in the ^1H spectrum as three overlapping doublets of doublets ($^3J_{HH}$ 7.1, $^3J_{PH}$ 14.3 Hz) centered at δ_H 1.78 ppm, and the CH proton is seen as a multiplet at δ_H 5.16 ppm, which is presumably three doublets of quartets with a small $^2J_{PH}$ coupling constant because, in the $^1H–\{^{31}P\}$

Scheme 1.



spectrum, there is no significant change in the CH proton pattern.

An NMR investigation of a 1:1 reaction of **I** with Na_2SO_3 in D_2O at room temperature (r.t., ~295 K) under Ar revealed that the phosphine **II**-d_3 is formed initially in the first stage; the reaction stoichiometry is presumably that shown in Eq. 3, which has been established for $(HOCH_2)_3P$ {Eq. (3), with Me replaced by H [8, 20, 33]}; the deuteroxymethane-sulfonate salt is formed via the reaction of HSO_3^- with acetaldehyde. However, unlike $(HOCH_2)_3P$ which is stable under such conditions, the phosphine **II**-d_3 partially decomposes to the deuterated bis(α-hydroxyethyl) phosphine $[DO(Me)CH]_2PD$ (**III**-d_3) and acetaldehyde [Eq. (4)]. In the $^{31}P–\{^1H\}$ spectrum recorded after 15 min, **II**-d_3 is seen as the expected two singlets (Scheme 1) at δ_P 8.4 and 7.1 ppm in a 1:3 ratio (Fig. 1a). The phosphine **III**-d_3 is seen as three triplets at δ_P –26.8, –28.5 and –31.6 ppm ($^1J_{PD}$ 33 Hz) in a 1:2:1 ratio (Fig. 1a), instead of the expected two 1:1 resonances for the (*RR*)/(*SS*) and (*RS*)/(*SR*) diastereomers (Scheme 1). A plausible rationalization is that in the (*RS*)/(*SR*) enantiomers, the P-atom is chiral because the hydroxyethyl groups with (*R*)- or (*S*)-chirality are different, and so this generates two (*RSR*) and (*SRS*) enantiomers that are apparently not NMR-identical. Of interest, only one δ_P 15.6 ppm resonance was given for $[HO(Cl_3C)CH]_3P$, and this was assigned to a preferred (*RRR*)/(*SSS*) diastereomer of just two considered possibilities: (*RRR*)/(*SSS*) and (*RRS*)/(*RSS*) [24]. In the ^1H spectrum, the CH protons of **II**-d_3 and **III**-d_3 appear as a broad multiplet at δ_H 4.69–4.43 ppm, which overlaps with the CH resonance of $DO(Me)C(H)SO_3Na$, and a doublet of quartets at δ_H 4.38 ppm ($^3J_{HH}$ 7.3 and $^2J_{PH}$ 1.9 Hz), which is assigned to one of the **II**-d_3 diastereomers.

$$[DO(Me)CH]_4P^+Cl^- + Na_2SO_3 \longrightarrow [DO(Me)CH]_3P + DO(Me)C(H)SO_3Na + NaCl \quad (3)$$

$$\underset{\textbf{II}\text{-}d_3}{[DO(Me)CH]_3P} \rightleftharpoons \underset{\textbf{III}\text{-}d_3}{[DO(Me)CH]_2PD} + MeCHO \quad (4)$$

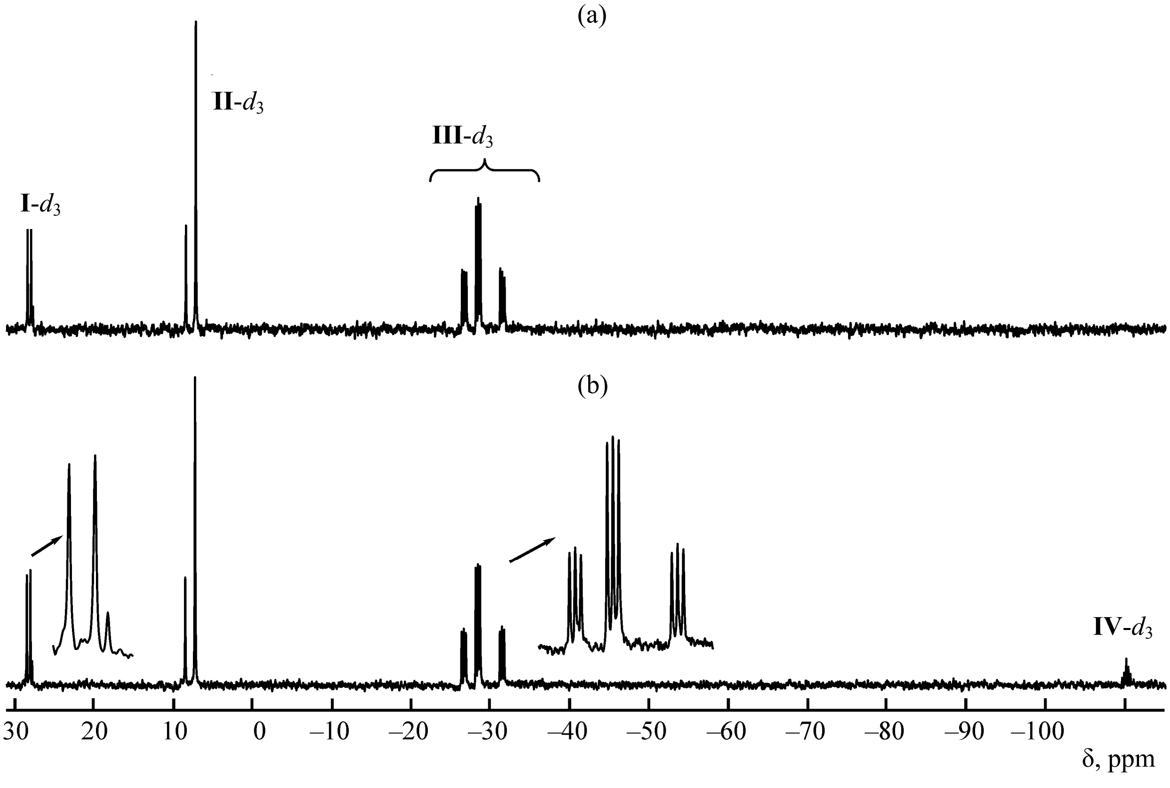


Fig. 1. The $^{31}P–\{^1H\}$ spectrum of the reaction of **I** (present as **I**-d_4) and Na_2SO_3 (1:1, Ar, D_2O, r. t.) after: (a) 15 min; (b) 1 day.

The Me resonances of both phosphines form a broad multiplet at δ_H 1.60–1.40 ppm. The CH and Me protons of the deuteroxymethane-sulfonate anion, $DO(Me)C(H)SO_3^-$, are seen as a quartet at δ_H 4.60 and a doublet at 1.51 ppm ($^3J_{HH}$ 6.6 Hz), respectively. Acetaldehyde (δ_H 9.70 quartet, 2.27 doublet, $^3J_{HH}$ 3.0 Hz) and its diol, present as $MeCH(OD)_2$ (δ_H 5.27 quartet, 1.35 doublet, $^3J_{HH}$ 5.2 Hz), are also observed.

After 1 day, the ^{31}P–{^1H} spectrum (Fig. 1b) revealed a quintet at δ_P −110.2 ppm ($^1J_{PD}$ 32 Hz) assignable to deuterated mono(α-deuteroxyethyl)phosphine $[DO(Me)CH]PD_2$ (**IV**-d_3), the disproportionation product of **III**-d_3 [Eq. (5)]. Use of a 2-fold excess of Na_2SO_3 (D_2O, r.t., Ar) completely consumed the **I**-d_4 in 20 min, when **II**-d_3 and **III**-d_3 were present in a ratio of 4:5; the acetaldehyde was detected only as the diol.

$$\underset{\textbf{III}\text{-}d_3}{[DO(Me)CH]_2PD} \rightleftharpoons \underset{\textbf{II}\text{-}d_3}{[DO(Me)CH]_3P} + \underset{\textbf{IV}\text{-}d_3}{DO(Me)CHPD_2} \qquad (5)$$

Neutralization of the chloride **I** with Et_3N (1:1 or 1:2, r.t., Ar, D_2O) also leads to a mixture of **II**-d_3 and **III**-d_3, but now in a 2:1 ratio because the equilibrium of Eq. (4) is shifted to the **II**-d_3 side in the absence of the SO_3^{2-} that scavenges the acetaldehyde under these conditions [see Eq. (3)].

The instability of **II**, the first reported homolog of the widely used $(HOCH_2)_3P$, in aqueous media (and almost certainly in organic media) is consistent with reported data that steric hindrance prohibits formation of tris- and tetrakis(α-hydroxyalkyl)phosphorus derivatives [13]. The instability is also consistent with our findings that electron-donor groups facilitate decomposition of (α-hydroxyalkyl)phosphines [30, 31]. Consistent with this, the use of the electron-accepting CCl_3 group generates the stable, but water-insoluble, tris(α-hydroxyalkyl)phosphine $[HO(Cl_3C)CH]_3P$ [24].

A 1:1 mixture of **I** and $NaHSO_3$ (D_2O, Ar, r.t.) shows no immediate reaction, as reported for the corresponding $(HOCH_2)_4PCl$ system [33]. After 30 min in a 1:4 chloride **I** and $NaHSO_3$ reaction, the ^{31}P–{^1H} spectrum revealed two equal intensity triplets at δ_P 50.1 and 48.3 ppm with $^1J_{PD}$ 72 Hz (Fig. 2a); these are assigned to the two diastereomers of the deuterated bis(α-hydroxyethyl)phosphine oxide $[DO(Me)CH]_2P(O)D$ (**V**-d_3), the $^1J_{PD}$ value being essentially the same as that found for $[DOCH_2]_2P(O)D$ [33]. The triplets were slowly replaced over a day by two 1:1 singlets seen first at δ_P 44.8 and 43.8 ppm (Fig. 2a), but over 2 days these shift downfield by ~2 ppm (Figs. 2b, 2c); at this stage, only these two singlets could be seen along with the small δ_P 64.4 and 62.9 ppm signals that are assigned to the sulfide $[DO(Me)CH]_3PS$ (see below). The new singlets, because of the absence of $^1J_{PD}$ coupling, are assigned to the phosphinic acid derivative $[DO(Me)CH]_2P(O)OD$ (**VI**-d_3), the oxidation product of **V**-d_3, and the 1:1 intensities are consistent with the presence of just the two chiral C-centers. The ^1H data (see below) are also consistent with the loss of two aldehyde equivalents from the chloride **I**-d_4 in that the final $DO(Me)C(H)SO_3Na$: **VI**-d_3 ratio is 2:1.

In the ^1H spectrum of **V**-d_3, instead of the anticipated two sets of resonances due to two diastereomers, three types of DO(Me)CH moieties were detected. Multiplets of the CH and Me protons, centered at δ_H 4.50 and 1.60 ppm, respectively (Fig. 3), were simulated as three overlapping AM_3X spin systems using: (a) (a) J_{AM} 7.3, J_{AX} 4.2, J_{MX} 16.0 Hz; (b) J_{AM} 7.3, J_{AX} 4.6, J_{MX} 16.0 Hz; and (c) J_{AM} 7.3, J_{AX} 1.9, J_{MX} 15.5 Hz (in all cases X is the P-atom). This ^1H pattern implies that the HO(Me)CH groups of one diastereomer are anisochronous ($\Delta \sim 4$ Hz). The Me protons of two diastereomers of **VI**-d_3 are seen at δ_H 1.45 and 1.43 ppm (Fig. 4) as two doublets of doublets ($^3J_{HH}$ 7.1, $^3J_{PH}$ 14.8 Hz and $^3J_{HH}$ 7.3, $^3J_{PH}$ 14.3 Hz, respectively), while the CH protons are seen as two overlapping quartets at δ_H 4.22 and 4.19 ppm (implying no measurable $^2J_{PH}$ coupling). After 30 min, both $DO(Me)C(H)SO_3Na$ and acetaldehyde diol were detected, whereas only the sodium salt was observed after 1 day. It should be noted that after 2 h of reaction, an off-white suspension of elemental sulfur appeared; the S_8 could be identified by its characteristic fragmentation pattern in a low-resolution EI mass spectrum [37]. The increasing presence of the suspension could well give rise to the minor shifts in the NMR spectra. The observed changes (carried out under Ar) are outlined in Scheme 2, although the source of the [O] required for the oxidation is unclear; trace O_2 is considered unlikely, and the well established OH^- oxidation of phosphines with co-generation of H_2 [15, 21, 38] seems more plausible.

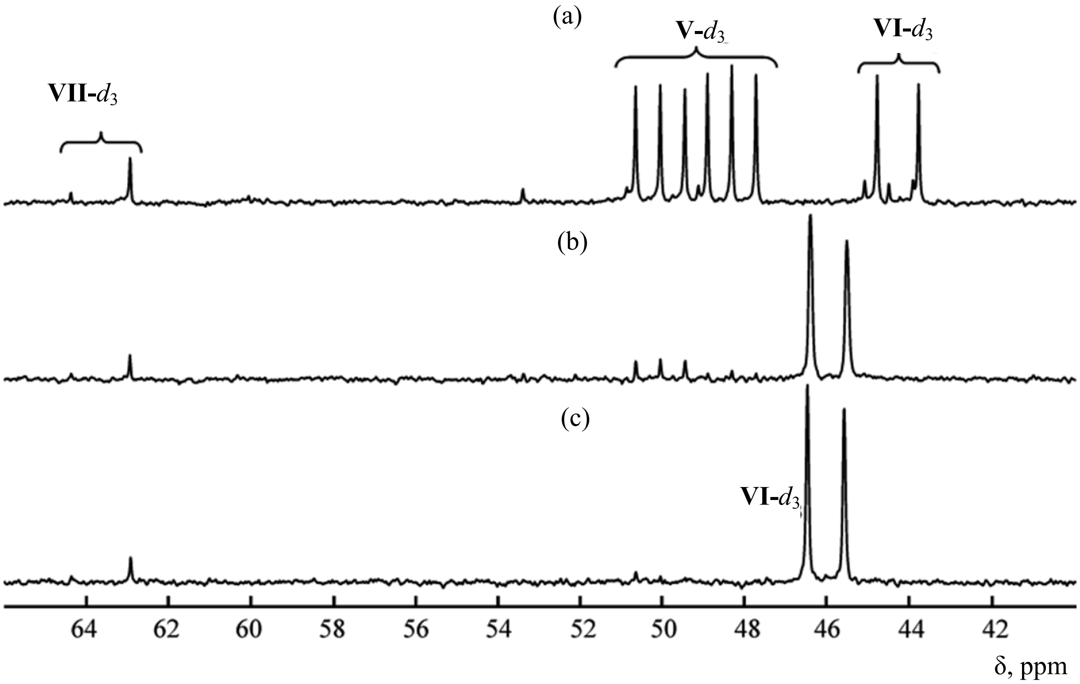


Fig. 2. The $^{31}P-\{^1H\}$ spectrum of the reaction of **I** (present as **I**-d_4**)** and $NaHSO_3$ (1:4, Ar, D_2O, r. t.) after: (a) 30 min; (b) 1 day; and (c) 2 days.

The earlier reported [33], corresponding slow oxidations under Ar of $(HOCH_2)_4PCl$ to give the oxide and phosphinic acid derivative are similarly poorly understood. It should also be noted that, in the reaction of PH_3 with benzaldehyde in basic conditions, a transfer of the carbon-oxygen to the phosphorus with the formation of a phosphine oxide or phosphinic acid can take place [39, 40] but, in the presence of $NaHSO_3$, any acetaldehyde present would form $DO(Me)C(H)SO_3^-$ and prevent any such oxidation process.

In a reaction of **I** with $Na_2S_2O_3$ in D_2O (1:1, Ar, r.t.), the $^{31}P\{^1H\}$ resonances of **I**-d_4 are replaced within 15 min by two lower field singlets at δ_P 64.4 and 62.9 ppm in a diastereomeric ratio of 1:3.5 (see also Fig. 2). These singlets are assigned to the sulfide $[DO(Me)CH]_3PS$ (**VII**-d_3), formed according to Eq. (6), by analogy with

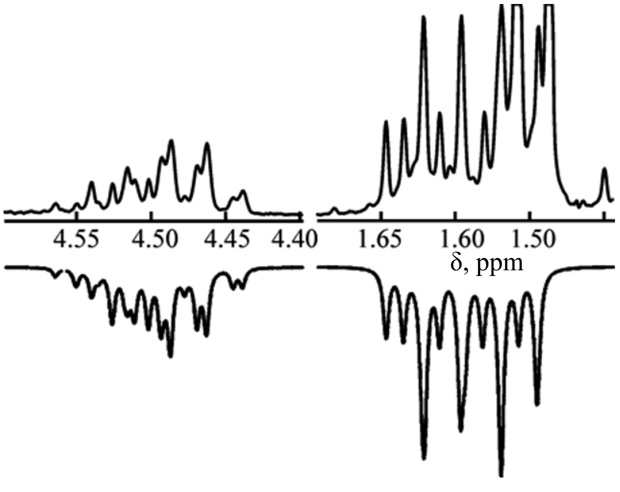


Fig. 3. The experimental (top) and simulated (bottom) AM_3X ^1H NMR patterns (X = P) for the CH and Me protons of **V**-d_3.

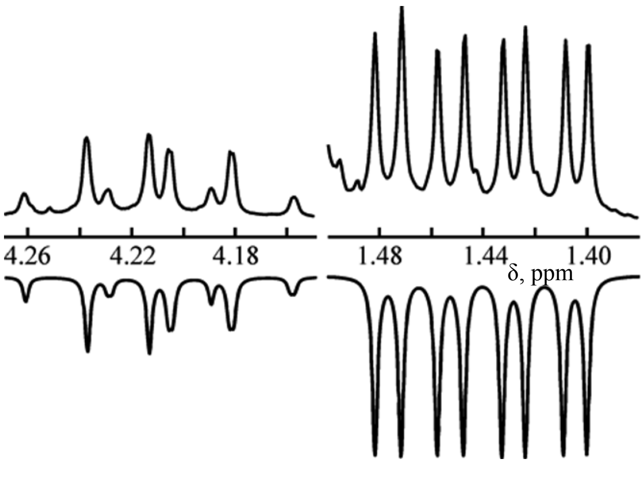
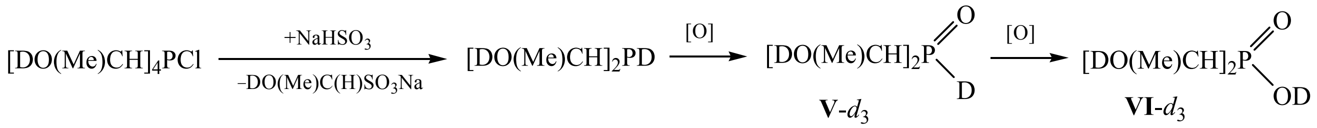


Fig. 4. The experimental (top) and simulated (bottom) AM_3X ^1H NMR patterns (X = P) for the CH and Me protons of **VI**-d_3.

Scheme 2.



$$[DO(Me)CH]_4PCl \xrightarrow[-DO(Me)C(H)SO_3Na]{+NaHSO_3} [DO(Me)CH]_2PD \xrightarrow{[O]} \underset{\mathbf{V}\text{-}d_3}{[DO(Me)CH]_2P(=O)D} \xrightarrow{[O]} \underset{\mathbf{VI}\text{-}d_3}{[DO(Me)CH]_2P(=O)OD}$$

the corresponding reaction of $(HOCH_2)_4PCl$ with $Na_2S_2O_3$ under the same conditions [33]. The ratio of the (*RRR*)/(*SSS*) and [(*RRS*)/(*RSS*), (*RSS*)/(*SRR*), (*RSR*)/(*SRS*)] diastereomers is close to the expected 1:3 for three identical chiral centers (see Scheme 1). However, the ^1H spectrum (Fig. 5, top) is surprisingly complex, but can be simulated (Fig. 5, bottom) as four equal intensity AM_3X spin systems for the CH and Me protons of four deuteroxyethyl groups (where X is a P-atom, J_{AM} 6.9, J_{AX} 2.0, J_{MX} 15.2 Hz), and an AM_3 spin system (J_{AM} 6.5 Hz) for DO(Me)C(H)SO_3Na. This implies that the P-atom of the (*RRS*)/(*RSS*), (*RSS*)/(*SRR*), and (*RSR*)/(*SRS*) enantiomers possesses one DO(Me)CH group of opposite chirality, and is thus prochiral, whereas the DO(Me)CH groups with the same chirality become NMR nonequivalent (anisochronous) and give rise to different ^1H resonances.

$$[DO(Me)CH]_4PCl + Na_2S_2O_3 \xrightarrow[D_2O]{} \underset{\mathbf{VII}\text{-}d_3}{[DO(Me)CH]_3PS} + DO(Me)C(H)SO_3Na + NaCl \qquad (6)$$

EXPERIMENTAL

Before use, distilled water and D_2O were stirred for 4 h under Ar. CD_3OD (Cambridge Isotope Laboratories) and EtOH were used as received, as were the Aldrich chemicals PH_3 (electronic grade) and acetaldehyde, and the Fisher Scientific products $Na_2S_2O_3$, Na_2SO_3, $NaHSO_3$, and 37% aq. HCl. 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. Elemental analyses were performed by M. Lakha on a Carlo Erba 1108 analyzer in the UBC department.

Preparation of [HO(Me)CH]$_4$PCl (I). PH_3 was bubbled for 1.5 h through an acetaldehyde (23 g) solution in air-free water (100 ml) with dropwise addition of HCl (37% aq., 52 ml). After removal of water, the white residue was recrystallized from a saturated solution in EtOH to give the chloride **I** in

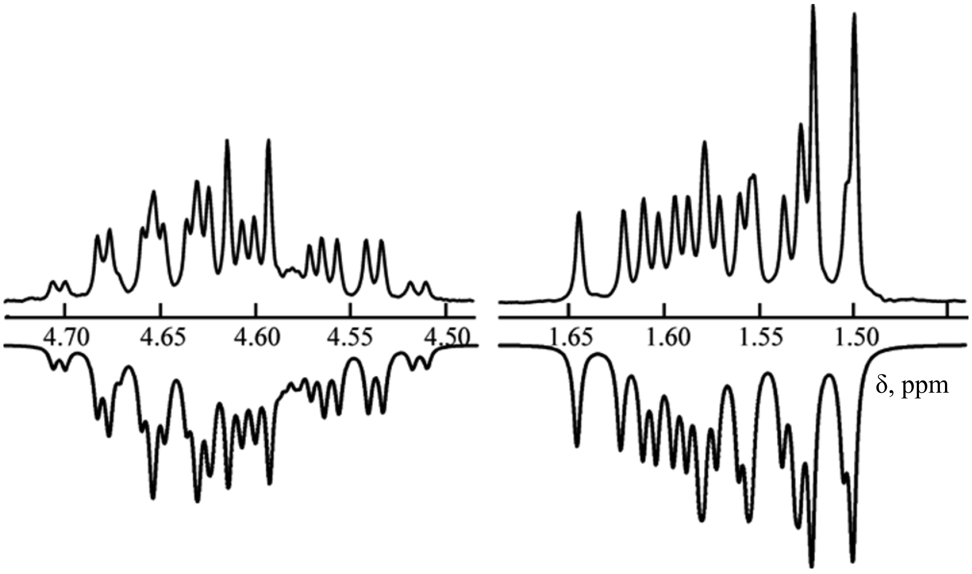


Fig. 5. The experimental (top) and simulated (bottom) AM_3X ^1H NMR patterns (X = P) for the CH and Me protons of **VII**-d_3; the spectra also include the AM_3 resonances for the CH protons (quartet at δ_H 4.60 ppm) and Me protons (doublet at δ_H 1.51 ppm) of DO(Me)C(H)SO_3^{2-}.

~80% yield. Found, %: C 39.3, H 7.8. $C_8H_{20}ClO_4P$. Calculated, %: C 38.95, H 8.17. The ^{1}H and ^{31}P–{^{1}H} NMR data are discussed in the text.

NMR investigation of a 1:1 reaction of the chloride I with Na_2SO_3. In a glove-box, **I** (30 mg, 0.12 mmol) was dissolved in a stirred, air-free D_2O solution (~1.5 ml) containing Na_2SO_3 (15.4 mg, 0.12 mmol). A sample of the solution (~0.7 ml) was then placed in a J-Young NMR tube and the spectra were recorded periodically at r.t. The same procedure was used for studying 1:1 reactions of **I** with Et_3N (12.3 mg, 0.12 mmol), $Na_2S_2O_3$ (19.2 mg, 0.12 mmol), and $NaHSO_3$ (12.7 mg, 0.12 mmol); reactions using stoichiometries other than 1:1 were studied similarly.

CONCLUSIONS

Tetrakis(α-hydroxyethyl)phosphonium chloride, $[HO(Me)CH]_4PCl$, is characterized for the first time by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, which reveals that the compound consists of three diastereomers in a 4:4:1 ratio. Reaction of $[HO(Me)CH]_4PCl$ with Na_2SO_3 or Et_3N in attempts to isolate $[HO(Me)CH]_3P$ leads to an equilibrium between this tertiary phosphine and the secondary phosphine $[HO(Me)CH]_2PH$. Except for $(HOCH_2)_3P$, tris(α-hydroxyalkyl)phosphines are generally unstable in aqueous media. Established also is that the water-soluble phosphinic acid $[HO(Me)CH]_2P(O)OH$ can be easily obtained by a 1:4 reaction of $[HO(Me)CH]_4PCl$ with $NaHSO_3$ (r.t., Ar), the secondary phosphine oxide $[HO(Me)CH]_2 \cdot P(O)H$ being an intermediate in this process. Interaction of $[HO(Me)CH]_4PCl$ with $Na_2S_2O_3$ affords the sulfide $[HO(Me)CH]_3PS$. Plausible rationales are presented for differences between the observed and theoretical/statistical diastereomeric ratios in the (α-hydroxyethyl)-containing phosphorus compounds.

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