Phosphorylating Power of Red Phosphorus towards Aldehydes in Basic and in Acidic Media

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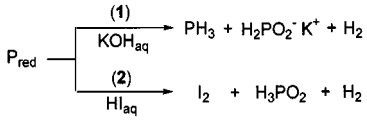
The reactivity of red phosphorus towards aldehydes was investigated under basic and acidic media. It was demonstrated that the real phosphorylating agent involved in the reaction was phosphane (PH_3) in basic media, and hypophosphorous acid (H_3PO_2) in acidic media. A convenient one-pot synthesis of (α-hydroxyalkyl)phosphinic acids from red phosphorus and aldehydes in basic media was realized under sonication. The same reaction under acidic media in the presence of hydriodic acid led to the corresponding phosphonic acids. The (α-hydroxyalkyl)phosphinic acids were readily prepared under sonication from hypophosphorous acid and aldehydes in the presence of catalytic amounts of hydrochloric acid. The mechanism of the addition reaction of PH_3 to benzaldehyde was elucidated and shows the complexity of the reaction as a function of the experimental conditions.

Introduction

The preparation of organophosphorus compounds from elemental phosphorus and in particular from red phosphorus (allotropic amorphous form), which is safe and easily handled, is of synthetic interest. But the well-known very low reactivity of red phosphorus implies the use of drastic conditions and a catalytic amount of an activating agent.[1][2]

Our previous studies have been focused on the investigation of the reactivity of amorphous red phosphorus.[3][4] We have demonstrated that its basic hydrolysis allows the generation of PH_3, hydrogen and hypophosphite ion (Scheme 1; pathway 1).[3] Thus, the synthesis of aliphatic and vinylic phosphane derivatives can be realized by a one-pot reaction from red phosphorus and terminal alkenes and alkynes in basic media under sonication.[3] The reaction involves the addition of the in situ generated PH_3 to unsaturated compounds and occurs by a Michael-like reaction mechanism (Pudovik reaction).



Scheme 1. Oxido-reductive disproportionation of red phosphorus in basic and acidic media

Furthermore, we have shown that acid hydrolysis of red phosphorus in the presence of hydriodic acid afforded iodine, hydrogen and hypophosphorous acid by an oxido-reductive disproportionation (Scheme 1; pathway 2).[4] In spite of the complexity of the hydrolysis reaction of elemental phosphorus, due to the large number of oxidized and reduced states, the explanation of its reactivity can be deduced from the dismutation equilibrium between elemental phosphorus, phosphane and hypophosphorous acid (Scheme 2).

Scheme 2. Dismutation equilibrium of red phosphorus in aqueous medium

Therefore, the stability of phosphane and hypophosphorous acid in water is dependent upon the acidity of the medium.[5] In strong acidic media (pH < 2), the hypophosphorous acid is stable and can appear as the preferential reducing agent while for other pH acidities, a competition between the phosphane and hypophosphite ion can arise.

Pursuing our investigation into the reactivity of red phosphorus[3,4] and P−H-labile derivatives,[6] and in view of the preparation of (α-hydroxyalkyl)phosphorus derivatives, we wish to report the reactivity of red phosphorus towards aldehydes in basic and acidic media. In recent years, the preparation of α-hydroxyphosphoryl derivatives (phosphonic and phosphinic acids, esters and salts) has attracted significant attention due to their potential biological activity,[7−11] their usefulness as extractants,[12] antipyretics,[12] and intermediates in the synthesis of other α- and γ-substituted phosphorus compounds.[13] Known preparations of (α-hydroxyalkyl)phosphorus acids include Pudovik addition reactions of dialkyl-H-phosphonates, phosphites or phosphanes to carbonyl compounds under base-catalyzed conditions,[14−19] or under anhydrous strongly acidic conditions.[20−21]

In contrast to the well-documented reactivity of red phosphorus in basic medium,[3][22] few examples concerning its reactivity in acidic medium have been described. The unique example of the synthesis of organophosphorus derivatives from red phosphorus in acidic medium is related to the electrolysis of a suspension of red phosphorus in al-

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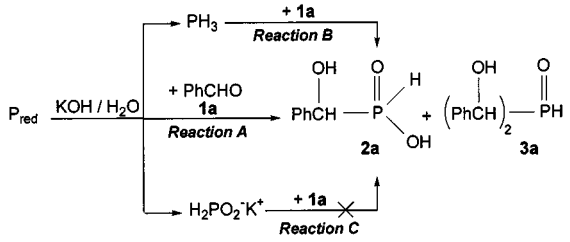
cohols under continuous introduction of HCl gas leading to the corresponding organophosphates.[2a,23]

In order to determine the nature of the phosphorus intermediate which is present in each medium, and to estimate their synthetic interest as cheap and safe raw materials upon the preparation of free (α-hydroxyalkyl)phosphorus acids, we have compared the reactivity of PH_3 and hypophosphorous acid towards aldehydes in basic and acidic media.

Results and Discussion

I. Reactivity of Red Phosphorus Towards Aldehydes in Basic Media

When a heterogeneous mixture of red phosphorus and benzaldehyde (**1a**) in basic media (KOH/H_2O/DMSO) was subjected to ultrasonic irradiation (20 kHz) for 10 min, the reaction mixture exhibited the presence of the potassium salt of mono(α-hydroxybenzyl)phosphinic acid (**2a**) [$\delta^{31}P$ = 24.4 (dd, $^1J_{PH}$ = 485 Hz, $^2J_{PCH}$ = 11 Hz)] and bis(α-hydroxybenzyl)phosphane oxide (**3a**) [$\delta^{31}P$ = 21.1 and 21.4 (dt, $^1J_{PH}$ = 486 Hz, $^2J_{PCH}$ = 13 Hz) with a diastereomeric ratio 1:1] in the ratio **2a/3a** = 2:1, and potassium hypophosphite [$\delta^{31}P$ = 0.9 (t, $^1J_{PH}$ = 480 Hz)] (Scheme 3; Reaction A). Compound **2a** was isolated in the acid form in 20% yield.



Scheme 3. **Reaction A**: one-pot pathway from P_{red}/ultrasound/10 min; **Reaction B**: two-steps pathway from PH_3/30°C/2.5 h; **Reaction C**: from $H_2PO_2^-K^+$/ultrasound/10 min; **A**, **B**, **C**: DMSO/KOH/H_2O

As in the case of alkenes and alkynes,[3] we have demonstrated that the one-pot synthesis of (α-hydroxybenzyl)-phosphinic acid (**2a**) from red phosphorus and **1a** involves the in situ generation of PH_3 as phosphorylating agent. Actually, the reaction occurs in a two-step pathway (from PH_3 generated by alkaline hydrolysis of the red phosphorus or by acid hydrolysis of zinc phosphide) leading to **2a** and **3a** in the ratio **2a/3a** = 1:1 (Scheme 3; Reaction B), whereas it fails from hypophosphite ions under the same conditions (Scheme 3; Reaction C).

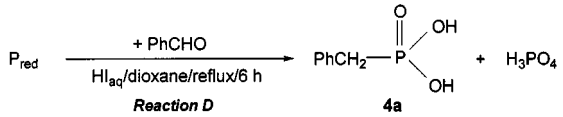
This procedure (Scheme 3; Reaction A) applied to aromatic and α,β-unsaturated aldehydes such as 4-methylbenzaldehyde or cinnamaldehyde affords the corresponding mono- and bis(α-hydroxyalkyl)phosphinic acids **2**−**3** in the same ratio and yields than with benzaldehyde, but it fails with aliphatic examples bearing long chains (C_8−C_{12}) due to their foaming power under sonication and the formation of by-products in basic media.

The rearrangement α-hydroxyphosphonate to phosphate in basic media is not observed,[16a,24,25] and the isolated (α-hydroxybenzyl)phosphinic acid (**2a**), kept in the presence of KOH/H_2O/DMSO, remains unchanged at room temperature for two weeks.

Thus, the fast one-pot synthesis of (α-hydroxyalkyl)phosphinic acid from red phosphorus and aldehydes in basic media under sonication is an attractive synthetic method for aromatic aldehydes but it does not apply to aliphatic examples due to the formation of many by-products.

II. Reactivity of Red Phosphorus towards Aldehydes in Acidic Media

Preparation of PH_3 by electrolytic reduction[26] of elemental white phosphorus or by its thermal acid-catalyzed dismutation at 280°C via red phosphorus as the intermediate was reported.[27] Thus, the electrochemical synthesis of (α-hydroxyalkyl)phosphane oxides from white phosphorus by in situ generation of PH_3 has been realized.[27] On the other hand, the reducing character of red phosphorus in acidic aqueous media has been related to the generation of hypophosphorous acid,[4] so the question of the reactivity of red phosphorus in acidic media, its ability to react with unsaturated compounds and in particular the nature of the phosphorylating agent involved under these conditions, arises. For comparison, we chose the same reaction of red phosphorus with benzaldehyde (**1a**) in basic media, but in dioxane and in the presence of 57% aqueous hydriodic acid under reflux for 6 h (Scheme 4; Reaction D).



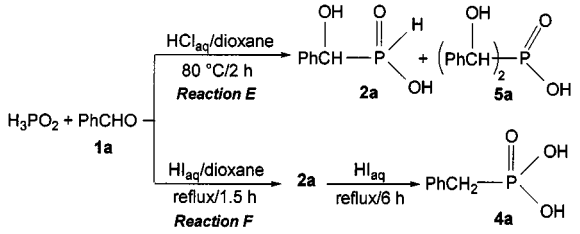
Scheme 4. Reactivity of red phosphorus towards benzaldehyde in acidic medium

The reaction leads to benzylphosphonic acid (**4a**) [$\delta^{31}P$ = 31.0 (t, $^2J_{PCH}$ = 20 Hz); 20%] and orthophosphoric acid (80%). When hydrochloric acid (35%) is used instead of hydriodic acid, the reaction gives phosphoric acid and only traces of **4a** as minor product are observed by ^{31}P NMR. This phenomenon can be attributed to the ability of these two acids to dissociate to hydrogen and iodine or chlorine, and their redox potentials (Cl_2/Cl^- = 1.358 V; I_2/I^- = 0.621 V).[28] The reaction also occurs with 4-methylbenzaldehyde (**1b**) under the same conditions as for **1a** but it fails with aliphatic aldehydes.

Although the efficiency of ultrasound is well known in the case of heterogeneous reactions,[3,6,29] we could not perform the reaction under ultrasonic irradiation using a 20-kHz probe (13 mm diameter) dipping in the reactor, due to the corrosive mixture. The use of an ultrasonic bath, "cup horn" probe, does not improve either the rate or the yield of the reaction.

In order to explain the mechanism of the formation of **4a**, the reaction of hypophosphorous acid and benzal-

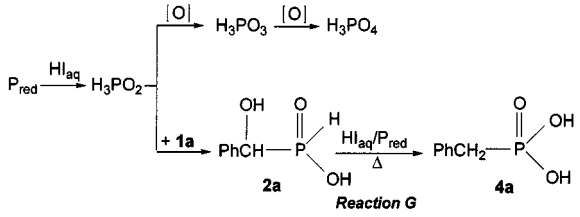
dehyde (**1a**) was conducted in dioxane in the presence of hydrochloric acid under heating at 80°C for 2 h (Scheme 5; Reaction E), and in the presence of hydriodic acid under heating (Scheme 5; Reaction F).



Scheme 5. Influence of the redox potentials of acids upon the addition reaction of the hypophosphorous acid to benzaldehyde

By reaction E, mono(α-hydroxybenzyl)phosphinic acid (**2a**) (main product, 68%) and bis(α-hydroxybenzyl)phosphinic acid (**5a**) (25%) were obtained and isolated. The use of an excess of hypophosphorous acid (3 equiv.) avoids the formation of bis-adduct **5a**. When the reaction was carried out in the presence of hydriodic acid under heating, we observed by ^{31}P-NMR spectroscopy of the reaction mixture the formation of **2a** (1.5 h) which disappeared with time in favor of **4a** (6 h). The reduction of the hydroxy function of α-hydroxy ketones by HI$_{aq}$ has been reported.[12a] Actually, we have verified that the isolated **2a** undergoes reduction of the α-hydroxy function with concomitant oxidation of the P−H bond in the presence of the couple "HI$_{aq}$/P$_{red}$" under reflux for 6 h and affords the phosphonic acid **4a** (Scheme 6; Reaction G).

Consequently, the reaction of the couple "HI$_{aq}$/P$_{red}$" with benzaldehyde in the presence of hydriodic acid involves the in situ generation of hypophosphorous acid which is the phosphinylating agent. It simultaneously undergoes an oxidation reaction to give phosphorous and phosphoric acids and an addition reaction with benzaldehyde affording (α-hydroxybenzyl)phosphinic acid (**2a**) which leads to **4a** by a reduction-oxidation in the presence of HI$_{aq}$ (Scheme 6).

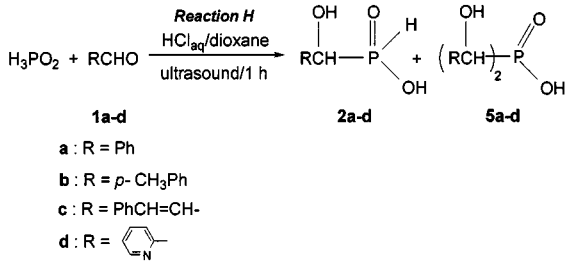


Scheme 6. Evidence of the phosphorylating and reductive properties of the couple "P$_{red}$/HI$_{aq}$"

III. Synthesis of α-Hydroxyalkylphosphinic Acids from Hypophosphorous Acid

Our study on the reaction mechanism of red phosphorus reactions in acidic media brought us to investigate the reactivity of hypophosphorous acid towards aldehydes. The addition reaction of hypophosphorous acid to carbonyl compounds has already been described in the literature.[30][31] The reaction often requires crystalline hypophosphorous acid and occurs upon prolonged heating under acid catalysis to afford mono- and bis(α-hydroxyalkyl)phosphinic acids.

We have optimized the reaction conditions by use of commercially available 50 wt.-% aqueous hypophosphorous acid, catalytic amounts of hydrochloric acid and ultrasonic irradiation which reduces the reaction time to 1 h. We have then extended our optimized synthetic method for preparation of (α-hydroxybenzyl)phosphinic acid from hypophosphorous acid to other aromatic and α,β-unsaturated aldehydes (Scheme 7; Reaction H).



Scheme 7. Synthesis of (α-hydroxyalkyl)phosphinic acids from hypophosphorous acid

Indeed, the reaction of 50 wt.-% aqueous hypophosphorous acid with 1.2 equivalents of aldehyde in the presence of 0.2−0.5 equivalent of hydrochloric acid in dioxane under sonication for 1 h affords mono(α-hydroxyalkyl)phosphinic acids **2a−d** as the main products (58−68%) accompanied by the corresponding bis-adducts **5a−d** (10−25%), except for the 2-pyridinecarbaldehyde where the disubstituted acid **5d** is the main product (80%). The (α-hydroxyalkyl)phosphinic acids **2** and **5** were isolated and their respective yields are reported in the Experimental Section. However, in order to rigourously compare the selectivity of the addition reaction of the various aldehydes, the initial yields were estimated by ^{31}P-NMR analysis of the crude reaction mixtures prior to purification (Table 1).

For the mono(α-hydroxyalkyl)phosphinic acids **2a−d**, two diastereomers are expected due to the presence of two stereogenic centers: the carbon atom bonded to the phosphorus atom and the phosphorus atom bearing four different substituents. However, the phosphorus atom looses its stereogenic character due to the rapid prototropic transfer of the acidic proton between the phosphoryl (P=O) and the acid (P−OH) sites. Thus, the analysis of the ^{31}P-NMR spectra of **2a−d** gives rise to one signal at $\delta = 30$ (single signal for ^{31}P{^{1}H}-NMR spectra) with a large $^1J_{PH}$ of ca. 560 Hz.[32] For (α-hydroxyalkyl)phosphinic acids **2d** and **5d**, we observe a shielding of the chemical shifts ($\Delta\delta^{31}P \approx 11$) and a decrease of the coupling constants ($\Delta^1J_{PH} \approx 20$ Hz) which can be explained by the influence of the solvent (ethanol instead dioxane) and also by the electropositive charge upon the pyridinium moieties. The chemical shift of the signal of a carbon atom next to a phosphorus atom ($\delta^{13}C \approx 75$) and its coupling constant with the phosphorus atom ($^1J_{CP} \approx 105$ Hz) are consistent with the presence of an (α-hydroxyalkyl)phosphinic moiety. The methine proton

Table 1. Initial yields and NMR parameters of (α-hydroxyalkyl)phosphinic acids **2** and **5**

Compd.	R	Yield (%)[a]	$\delta^{31}P$ ($^1J_{PH}$)[b,c]	CH: $\delta^{13}C$ ($^1J_{CP}$)[c]	CH: δ^1H[c]
2a	Ph	68	31.9 (560 Hz)[b] 26.6 (517 Hz)[c]	76.3 (105 Hz)	4.73
5a		25	41.8, 40.6[b] (1:1)[d] 38.4[c]	70.6 (109 Hz)	5.15
2b	4-MeC_6H_4	66	32.1 (561 Hz)[b] 27.0 (511 Hz)[c]	74.3 (105 Hz)	4.87
5b		10	41.8, 40.8[b] (1:1)[d]	–	–
2c	PhCH=CH	58	31.9 (563)[b] 30.3 (522)[c]	70.2 (110 Hz)	4.50
5c		17	42.7, 41.8[b] (1:1)[d] 40.1, 38.8[c] (3:7)[d]	69.2 (104 Hz), 68.1 (106 Hz)	4.71, 4.61
2d	2-C_5H_4N	15	20.1 (539)[b]	–	–
5d		80	27.5; 26.4[b] (1:1)[d] 28.2; 26.8[c] (7:3)[d]	71.6 (105 Hz), 71.1 (105 Hz)	5.64, 5.55

[a] Yields of **2** and **5** determined by ^{31}P-NMR analysis of the crude reaction mixture. – [b] ^{31}P-NMR spectra of the crude mixture in "dioxane/H_2O", except for **2d** and **5d**: "EtOH/H_2O" due to the insolubility of the products in the medium. – [c] ^{31}P-, ^{13}C- and ^1H-(methine group) -NMR spectra of isolated products in D_2O (**2a**, **5d**), in CD_3COOD (**2b**), and in [D_6]DMSO (others). – [d] Ratio of diastereomers.

resonates in most cases as a doublet at $\delta \approx 4-5$ with $^2J_{HP}$ in the range of 8–9 Hz.

The bis(α-hydroxyalkyl)phosphinic acids **5a–d** exist as a 1:1 mixture of two diastereomers (*meso* and *d*,*l* form).[14c,32] The chemical-shift differences of the bis(α-hydroxyalkyl)-phosphinic acids are sufficient to permit accurate integration ($\Delta\delta^{31}P \approx 1$). The ratio of diastereomers established by ^{31}P-NMR spectroscopy is in good agreement with the values obtained by ^1H-NMR spectra (Table 1). The bis(α-hydroxyalkyl)phosphinic acid **5d** bearing two pyridine moieties is a new water-soluble phosphinic acid which can be viewed as good chelating agent which may have utility in NMR imaging,[33] and in biological screenings.[34] The α-aminophosphonate analogs have been recently described.[18][35] The bis(α-hydroxyalkyl)phosphane oxide **3a** is oxidized to **5a** during purification and could not be isolated. However, as in the case of the bis(α-hydroxyalkyl)-phosphinic acid **5**, the ^{31}P-NMR analysis of **3a** exhibits the presence of two signals instead of the expected three. Degeneracies may occur in basic media by rapid "phosphinate/phosphinite" equilibrium excluding the stereogenic center (phosphorus atom).[32]

IV. Reactivity of PH_3 towards Aldehydes in Acid Media

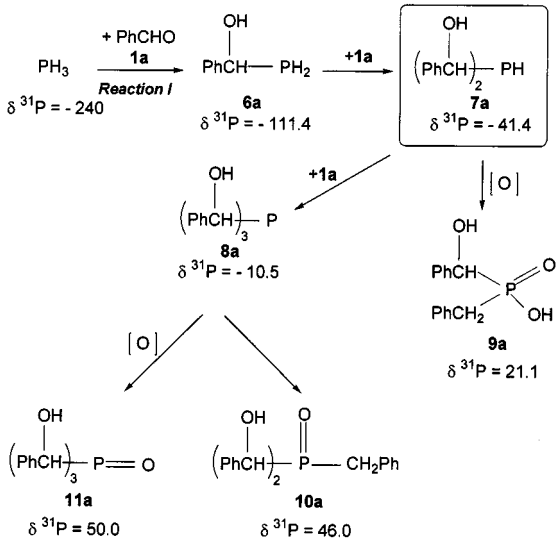
Phosphonium salts have been widely studied and have attracted significant interest due to their numerous applications.[12][36] Examples of formation of (α-hydroxyalkyl)-phosphonium salts are considerably rarer. Such compounds have been synthesized from the nucleophilic addition of a phosphane to carbonyl compounds in the presence of electrophilic trapping agents.[12,36,37] The reactions of PH_3 with aldehydes yield various products depending on their structure, the catalysts, and the solvent. Thus, the corresponding phosphonium salts are obtained from formaldehyde whereas with other aldehydes various compounds are formed.[13a,14b] The pecularity of these reactions is mostly due to transformations of unstable intermediates resulting from condensation of one or two aldehyde molecules with PH_3. Thus, the reaction of benzaldehyde with PH_3 has been surrounded by controversy since it was initially proposed that the phosphonium salt was the adduct of the reaction when conducted in ether.[38] Tris(α-hydroxybenzyl)phosphane has also been assigned to the same adduct.[39] Finally, the compound was determined to be benzyl bis(α-hydroxybenzyl)phosphane oxide, whose formation involves the transfer of the oxygen atom from the carbon to the phosphorus atom.[40] The primary phosphane oxide has been proposed as intermediate.[40b]

Furthermore, benzaldehyde reacts differently with phosphane (PH_3) in alcoholic solution and affords bis(α-ethoxybenzyl)phosphane in ethanol via a hemiacetal intermediate.[39]

Taking into account that most of these adducts have many applications particularly as intermediates for organic synthesis, as fungicides or as extractants of metal ions, and the fact that PH_3 is one of the hydrolysis products of red phosphorus, we attempted to elucidate the mechanism of the reaction of PH_3 with aldehydes.

Phosphane (PH_3), generated by basic hydrolysis of red phosphorus or by acid hydrolysis of zinc phosphide, is passed through an acidic solution of benzaldehyde in dioxane/hydrochloric acid maintained at 30°C (Scheme 8; Reaction I). (The reaction occurs slowly in the absence of acid catalyst.) The reaction mixture exhibited the presence of (α-hydroxyalkyl)phosphanes **6–8a** and their corresponding oxidized derivatives **9–11a** after 2 h. The ^{31}P-NMR spectrum of the main product ($\delta^{31}P = -41.4$) appears as a doublet of triplet with $^1J_{PH} = 208$ Hz and $^2J_{PCH} = 18$ Hz. The negative sign of its chemical shift, its multiplicity (dt) and the $^1J_{PH}$ value are consistent with a trivalent P–H phosphorus atom, the secondary phosphane **7a** (Scheme 8). This is consistent with the data provided by the mass spectrum of the mixture (*m*/*z* = 247 $[M + 1]^+$). The $^{31}P\{^1H\}$-NMR spectrum of **7a** exhibits a single signal at $\delta = -41.4$,

whereas the molecule has two stereogenic carbon centers and a stereogenic phosphorus center and, consequently, it must exist in three diastereomeric forms as in the case of phosphinic acids **5**. This paradoxical observation can be attributed to the rapid protonation/deprotonation of the phosphorus atom and to the low diastereotopic differences in the ^{31}P-NMR spectra of the phosphane **7a** in the presence of hydrochloric acid.[32][41]



Scheme 8. Evidence of the various steps upon the addition of PH_3 to benzaldehyde in acidic media

The detection of **7a** as intermediate in the reaction of PH_3 with benzaldehyde shows that the transfer of the oxygen atom from the carbon to the phosphorus atom occurs upon the secondary phosphane and not on the primary phosphane as proposed previously.[40b] The phosphane **7a** is relatively stable in acidic solution but it decomposes during purification or upon evaporation of solvent. All attempts of complexation ($PdCl_2$, BH_3) or oxidation (S_8) of the phosphorus lone pair, rendering it more stable, were unsuccessful.

The ^{31}P-NMR and mass-spectra analysis of the mixture as a function of time shows the formation of phosphinic acid **9a** ($\delta^{31}P = 21.1$; $m/z = 263\ [M + 1]^+$) resulting from an α-hydroxy rearrangement followed by an oxidation of the P−H bond (Scheme 8). When the crude mixture is maintained under inert gas (argon), the phosphane **7a** undergoes a third addition of benzaldehyde and gives the tertiary phosphane **8a** ($\delta^{31}P = -10.5$; $m/z = 353\ [M + 1]^+$). This can then undergo either a rearrangement giving the tertiary phosphane oxide **10a** ($\delta^{31}P = 46.0$; $m/z = 353\ [M + 1]^+$) (already described by Buckler[40a]), or a slow oxidation at low temperature (−20 to 0°C) to afford tris(α-hydroxybenzyl)phosphane oxide (**11a**) ($\delta^{31}P = 50.0$; $m/z = 369\ [M + 1]^+$).

The follow-up of the reaction of PH_3 with benzaldehyde gives an explanation of the difficulties and the various structural interpretations of the adducts reported and to understand the mechanism involved (Scheme 8).

Conclusion

A simple and convenient route to free (α-hydroxyalkyl)-phosphinic acids starting from red phosphorus and aromatic or α,β-unsaturated aldehydes in basic media under sonication has been developed. It was clearly established that the phosphinylating agent under these conditions (basic media) is the in situ generated PH_3 and not hypophosphite.

In contrast to the case in basic media, the reaction of red phosphorus with aldehydes in acidic media involves the in situ generation of hypophosphorous acid, which is the phosphinylating agent. However, the redox disproportionation of red phosphorus requires the presence of aqueous hydriodic acid which reduces the α-hydroxy group and leads to phosphonic acids.

The reactivities of phosphane and hypophosphorous acid (actually the real phosphorylating agents involved in the reaction of red phosphorus with aldehydes in basic and in acidic media) towards aldehydes were studied. In particular, the reaction of hypophosphorous acid with aldehydes is optimized, since under the present conditions the (α-hydroxyalkyl)phosphinic acids can be readily prepared from aqueous hypophosphorous acid in the presence of catalytic amounts of hydrochloric acid. The ultrasonic irradition of the heterogeneous mixture reduces the reaction time to 1 h.

The mechanism of the addition of phosphane (PH_3) to benzaldehyde is studied by monitoring the reaction by ^{31}P NMR and MS. The secondary phosphane detected as the main product in the mixture is the reaction intermediate which can undergo various types of reactions as a function of experimental conditions.

Finally, this mechanistic study of the reaction of red phosphorus with aldehydes allowed us to develop new procedures for the synthesis of (α-hydroxyalkyl)phosphinic acids not only from inexpensive, non-toxic and non-flammable red phosphorus, but also from its hydrolysis product, hypophosphorous acid, and it tends to open new routes to the synthesis of important classes of compounds and to stimulate further research.

Experimental Section

General Comments: Spectra were recorded with the following instruments: IR spectra, Perkin−Elmer IRFT 1600; ^{1}H, ^{13}C and ^{31}P spectra, Bruker AC80, AC200 or 250WM; and mass spectra by chemical ionization (DCI/NH_3 or DCI/CH_4) or in positive FAB modes, Nermag R10−10H. Chromatographic separations were executed with Merck precoated preparative TLC plates on silica gel 60 F_{254}. Elemental analyses were performed by the Microanalytical Service Laboratory of the Laboratoire de Chimie de Coordination of Toulouse, France. The ultrasound generator was a 20-kHz generator (Bioblock−Vibracell 600 W) connected to a direct immersion horn (diameter 13 mm) dipping in a round-bottom cylindrical reactor. Red phosphorus (Prolabo), hypophosphorous acid (Aldrich), zinc phosphide (Strem), and aldehydes (Aldrich) were used as received from commercial suppliers without further purification.

General Procedures for the Synthesis of α-Hydroxyalkylphosphinic Acids

Reaction A: To a solution of red phosphorus (0.01 mol) in DMSO (6 mL) was added successively potassium hydroxide (17 mmol) in distilled H_2O (50 mmol) and aldehyde **1** (7.5 mmol). The mixture was sonicated for 10 min. After filtration of the excess of red phosphorus, the filtrate was acidified to pH = 2−3 with hydrochloric acid (37% aq) and extracted with chloroform.

Reaction B: The reaction was carried out under argon. Phosphane (PH_3) was generated by basic hydrolysis of red phosphorus or acid hydrolysis of zinc phosphide. To zinc phosphide (1.24 mmol) in distilled H_2O or red phosphorus (0.01 mol), stirred and heated at 50°C, was added dropwise an aqueous solution of sulfuric acid or potassium hydroxide. The generated phosphane was bubbled through the stirred solution of aldehyde **1** (7.5 mmol) and potassium hydroxide (9.6 mmol) in distilled H_2O (42 mmol) and DMSO (3.5 mL) at 30°C. The mixture was stirred and heated at 30°C for 2.5 h.

Reaction C: To a solution of 50% aqueous hypophosphorous acid (7.5 mmol) in DMSO (6 mL) was added KOH (17 mmol) in distilled H_2O (50 mmol) and benzaldehyde (**1a**) (7.5 mmol). The mixture was sonicated for 10 min. The ^{31}P-NMR spectrum of the reaction mixture showed the presence of (α-hydroxybenzyl)phosphinic acid (**2a**).

Reaction D: Red phosphorus (0.01 mmol) was added to a solution of aldehyde **1a** (0.01 mmol) in 57% aqueous hydriodic acid (3 mL). The mixture was heated under reflux for 6 h. The crude mixture was analyzed by ^{31}P-NMR spectroscopy. Since the initial yield of the organophosphorus compound was low, the reaction product was not isolated but identified by comparison with an authentic sample of benzylphosphonic acid prepared from (α-hydroxybenzyl)phosphinic acid (see Reaction G).

Reaction E: Hypophosphorous acid (50% aq) (4.3 mmol) was added to a solution of aldehyde **1a−d** (5.16 mmol) in dioxane (6 mL) and 37% aqueous hydrochloric acid (0.072 mL). The resulting heterogeneous mixture was stirred under reflux for 2−4 h or sonicated for 1 h. The work-up and purification of (α-hydroxyalkyl)phosphinic acids **2a−d** and **5a−d** vary as a function of the substituents.

Reaction F: To a solution of benzaldehyde (**1a**) (5.16 mmol) in 57% aqueous hydriodic acid (0.72 mL) and dioxane (6 mL) was added 50% aqueous hypophosphorous acid (4.3 mmol). The mixture was heated under reflux for 7 h. The progress of the reaction was monitored by ^{31}P NMR. (α-Hydroxybenzyl)phosphinic acid (**2a**) was initially formed (1.5 h), which disappeared as a function of time (6 h) in favor of benzylphosphonic acid (**4a**) (60%).

Reaction G: Red phosphorus (0.01 mmol) was added to a solution of (α-hydroxybenzyl)phosphinic acid (**2a**) (0.01 mmol) in 57% aqueous hydriodic acid (3 mL). The mixture was heated under reflux for 6 h.

Reaction H: The procedure occurs as Reaction E but the mixture was sonicated for 1 h instead of stirred under reflux.

Reaction I: Phosphane (PH_3) was generated as above. Then it was bubbled through the stirred solution of benzaldehyde (**1a**) (7.5 mmol) in dioxane (6 mL) and hydrochloric acid (37% aq) (0.72 mL) at 30°C for 2.5 h. The completion of the reaction was monitored by ^{31}P-NMR analysis.

Mono(α-hydroxybenzyl)phosphinic Acid (2a): This compound was obtained by reactions A, B, E, F, H. The residue obtained after concentration of the reaction mixture was taken up in chloroform. The precipitate that slowly formed in chloroform was filtered off and purified by chromatography (TLC plate, silica gel 60 F_{254}; eluent: MeOH/$CHCl_3$, 9:1). **2a** was purified as a white solid in 20% yield from the reaction A and 30% yield from the reaction H. R_f = 0.85 (MeOH/$CHCl_3$, 9:1); m.p. 107−108°C.[30][42] − ^{31}P NMR (32.44 MHz, D_2O): δ = 26.6 (d, $^1J_{PH}$ = 517 Hz, $^2J_{PH}$ = 9 Hz). − ^{1}H NMR (80.13 MHz, D_2O): δ = 7.46 (m, 5 H), 6.90 (dd, $^1J_{HP}$ = 515 Hz, $^3J_{HH}$ = 1 Hz, 1 H), 4.73 (dd, $^2J_{HP}$ = 9 Hz, $^3J_{HH}$ = 1 Hz, 1 H). − ^{13}C NMR (62,90 MHz, D_2O): δ = 132.40−129.40 (m), 76.30 (d, $^1J_{CP}$ = 105 Hz). − IR (KBr, cm^{-1}): ṽ = 3680−3600 (OH), 2324 (P−H), 1153 (P=O). − MS (DCI/NH_3); *m*/*z*: 174 $[M + 2]^+$.

Mono[α-hydroxy-α-(4-tolyl)methyl]phosphinic Acid (2b): This compound was obtained by reactions A and H (purified from reaction H). Solvents were removed under vacuum. The residue was taken up in distilled H_2O and extracted with chloroform. The aqueous layer was concentrated to dryness and the residue was taken up in the minimum of acetic acid. The excess of hypophosphorous acid precipitated in the mixture, and the supernatant layer was separated and then concentrated to dryness to give **2b** as a yellow paste in 30% yield. − ^{31}P NMR (32.44 MHz, CD_3COOD): δ = 27.0 (dd, $^1J_{PH}$ = 511 Hz, $^2J_{PH}$ = 8.5 Hz). − ^{1}H NMR (80.13 MHz, CD_3COOD): δ = 7.30−7.20 (m, 4 H), 7.00 (d, $^1J_{HP}$ = 511 Hz, 1 H), 4.87 (d, $^2J_{HP}$ = 8.7 Hz, 1 H), 2.07 (s, 3 H). − ^{13}C NMR (62.90 MHz, CD_3COOD): δ = 138.22 (s), 135.17 (s), 129.85 (m), 127.84 (m), 74.29 (d, $^1J_{CP}$ = 104.7 Hz), 55.79 (s). − IR (KBr, cm^{-1}): ṽ = 3527 (OH), 2298 (P−H), 1257.5 (P=O). − MS (DCI/NH_3); *m*/*z*: 185 $[M - 1]^+$, 138 $[M - H_2PO_2 + NH_3]^+$.

Mono(α-hydroxycinnamyl)phosphinic Acid (2c): This compound was obtained by reactions A and H (purified from reaction H). Solvents were removed under vacuum. After addition of distilled H_2O, products were extracted with diethyl ether and **5c** precipitated. To the resulting supernatant was added distilled H_2O. The aqueous layer was concentrated to dryness giving **2c** in 30% yield. M.p. 89−91°C. − ^{31}P NMR (81.015 MHz, [D_6]DMSO): δ = 30.3 (dd, $^1J_{PH}$ = 522 Hz, $^2J_{PCH}$ = 15 Hz). − ^{1}H NMR (80.13 MHz, [D_6]DMSO): δ = 7.60−7.20 (m, 5 H), 6.80 (d, $^3J_{HH}$ = 5 Hz, 1 H), 6.78 (d, $^1J_{HP}$ = 526 Hz, 1 H), 6.25 (ft, $^3J_{HH}$ = $^3J_{HP}$ = 5 Hz, 1 H), 4.50 (dd, $^2J_{HCP}$ = 12 Hz, $^3J_{HH}$ = 5 Hz, 1 H). − ^{13}C NMR (62.90 MHz, [D_6]DMSO): δ = 136.2 (s), 130.9 (s), 128.6 (s), 127.6 (s), 126.2 (s), 124.8 (s), 70.17 (d, $^1J_{CP}$ = 110 Hz). − IR (KBr, cm^{-1}): ṽ = 3384 (OH), 2515 (P−H), 1167 (P=O). − HRMS (glycerol; FAB < 0) for $C_9H_{11}O_3P$; *m*/*z*: calcd. 197.0367, found 197.0374 $[M - 1]^+$.

Bis(α-hydroxybenzyl)phosphane Oxide (3a): This diastereomer mixture was obtained by reactions A and B and was identified by the ^{31}P-NMR spectrum of the reaction mixture. − ^{31}P NMR (81.01 MHz, KOH/H_2O/DMSO): δ = 21.1 (dt, $^1J_{PH}$ = 486 Hz, $^2J_{PCH}$ = 13 Hz), 21.4 (dt, $^1J_{PH}$ = 486 Hz, $^2J_{PCH}$ = 13 Hz). − During the purification **3a** was oxidized to **5a**.

Benzylphosphonic Acid (4a): This compound was obtained by reactions D, F, G (purified from reaction G). After filtration of the excess of the red phosphorus, the filtrate was concentrated to dryness under vacuum. The residue was taken up with water, then the aqueous solution was extracted with diethyl ether. The aqueous layer was concentrated to dryness and the residue was recrystallized from isopropyl alcohol/acetone to afford benzylphosphonic acid (**4a**) as a white solid in 25% yield. − M.p. 164−166°C.[43] − ^{31}P NMR (32.44 MHz, D_2O): δ = 21.4 (t, $^2J_{PH}$ = 21.2 Hz). − ^{1}H NMR (80.13 MHz, D_2O): δ = 7.48 (m, 5 H), 3.25 (d, $^2J_{HP}$ = 20.7 Hz, 2 H). − ^{13}C NMR (62.90 MHz, CD_3OD): δ = 138.20 (s), 132.45(s), 131.43 (s), 129.07 (s), 38.77 (d, $^1J_{CP}$ = 127.4 Hz). − MS (DCI/NH_3); *m*/*z*: 172 $[M]^+$.

Bis(α-hydroxybenzyl)phosphinic Acid (5a): This compound was obtained by reactions A (from **3a**), E and H (purified from reaction H). Solvents were removed under vacuum. To the resulting residue was added toluene and the crude product was precipitated. The precipitate was separated from the supernatant and recrystallized from chloroform at low temperature in 15% yield as a white solid. − M.p. 192−193°C (from $CHCl_3$). − ^{31}P NMR (32.44 MHz, [D$_6$]DMSO): δ = 38.4 (m). − ^1H NMR (80.13 MHz, [D$_6$]DMSO): δ = 7.40−7.30 (m, 10 H), 5.15 (d, $^2J_{HP}$ = 7.4 Hz, 2 H). − ^{13}C NMR (62.90 MHz, [D$_6$]DMSO): δ = 138.7 (s), 128.9 (m), 70.6 (d, $^1J_{CP}$ = 108.8 Hz). − IR (KBr, cm^{-1}): ṽ = 3500−3000 (OH), 1162 (P=O). − MS (DCI/NH_3); *m/z*: 279 [M + 1]$^+$, 124 [PhCHOH + NH_3]$^+$. − $C_{14}H_{15}O_4P$·0.5 H_2O (287.237): calcd. C 58.54, H 5.61; found C 58.57, H 5.40.

Bis[α-hydroxy-α-(4-tolyl)methyl]phosphinic Acid (5b): This compound was obtained by Reaction H in 10% yield from the reaction mixture and could not be purified.

Bis(α-hydroxycinnamyl)phosphinic Acid (5c): This compound was obtained by reaction H. Solvents were removed under vacuum. After addition of distilled H_2O, products were extracted with diethyl ether. The organic layer was concentrated to dryness. Addition of *n*-hexane to the residue caused the formation of a precipitate which was separated from the supernatant and recrystallized from acetic acid at low temperature to obtain **5c** as a white solid in 16% yield. − M.p. 155−157°C (from CH_3COOH). − ^{31}P NMR (32.44 MHz, [D$_6$]DMSO): δ = 40.1 (m, 33%), 38.8 (m, 67%). − ^1H NMR (250.13 MHz, [D$_6$]DMSO): δ = 7.40−7.20 (m, 10 H), 6.70−6.40 (m, 4 H), 4.75−4.68 (m, 32%) + 4.65−4.58 (m, 68%) (2 H). − ^{13}C NMR (62.90 MHz, [D$_6$]DMSO): δ = 136.6 (s), 129.97 (s), 129.81 (s), 128.53 (s), 127.28 (s), 126.83 (s), 126.49 (s), 126.12 (s), 69.18 (d, $^1J_{CP}$ = 104.4 Hz), 68.13 (d, $^1J_{CP}$ = 105.6 Hz). − IR (KBr, cm^{-1}): ṽ = 3083−3000 (OH), 2836.5 (P−OH), 1069 (P=O). − HRMS (glycerol; FAB < 0) for $C_{18}H_{19}O_4P$; *m/z*: calcd. 329.0942, found 329.0937 [M − 1]$^+$. − $C_{18}H_{19}O_4P$ (330.302): calcd. C 65.45, H 5.76; found C 65.20, H 5.50.

Bis[hydroxy(2-pyridyl)methyl]phosphinic Acid Hydrochloride (5d): This compound was obtained by reaction H. Solvents were removed under vacuum. The residue was taken up in distilled H_2O and extracted with diethyl ether. The aqueous layer was concentrated to dryness. The residue was purified by successive recrystallization from ethanol at low temperature giving **5d** as a white solid in 35% yield. − M.p. 148−150°C (from EtOH). − ^{31}P NMR (32.44 MHz, D_2O): δ = 28.2 (67%), 26.8 (33%). − ^1H NMR (80.13 MHz, D_2O): δ = 8.77−7.89 (m, 8 H), 5.64 (d, $^2J_{HP}$ = 12 Hz, 61%) + 5.55 (d, $^2J_{HP}$ = 13 Hz, 39%) (2 H). − ^{13}C NMR (62.90 MHz, D_2O): δ = 155.8 (s), 148.6 (s), 143.2 (s), 128.2 (s), 127.9 (s), 71.6 (d, $^1J_{CP}$ = 104.6 Hz), 71.1 (d, $^1J_{CP}$ = 105.4 Hz). − IR (KBr, cm^{-1}): ṽ = 3751.5 (OH), 3080.5 (P−OH), 1159.5 (P=O), 1030.0 (C−N). − MS (MNBA; FAB > 0); *m/z*: 281 [M + 1]$^+$. − $C_{12}H_{15}Cl_2N_2O_4P$ (353.13): calcd. C 40.81, H 4.28, N 7.93; found C 41.10, H 4.07, N 7.85.

Bis(α-hydroxybenzyl)phosphane (6a): This compound was obtained by reaction I. It was stable in acidic solution but it decomposed during simple evaporation of the solvent. It could not be isolated but it was identified by ^{31}P-NMR and mass spectra. − ^{31}P NMR (32.44 MHz, dioxane/HCl): δ = −41.4 (td, $^1J_{PH}$ = 208 Hz, $^2J_{PH}$ = 18 Hz). − MS (glycerol; FAB > 0); *m/z*: 247 [M + 1]$^+$.

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