Dual Radical/Polar Pudovik Reaction: Application Field of New Activation Methods

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The Pudovik reaction (addition of organophosphorus compounds containing a labile P−H bond with alkenes and alkynes) can progess via a radical or (and) ionic mechanism. A comparative and systematic study including various reagents and different activation methods (heating, photochemical or ultrasonic irradiation, and dry medium supported reactions) is presented. Photolysis is the most efficient method for the radical processes, but in a few examples, ultrasonic irradiation can be more appropriate since the reaction time is shorter and ultrasound did not induce side-reactions (in particular *Z*/*E* isomerization). Dry medium process on basic solid support is the best anionic activation (yield, time, selectivity, purification facilities). Ultrasound, by its mechanical effects, can contribute to increase yield compared to the classical thermal method under these basic conditions. All the activation methods are efficient whatever the unsaturated substrates for the phosphine reactivity, whereas the appropriate activation method is exclusively determined by the nature of the unsaturated system for the thiophosphine (or phosphine oxide) reactivity.

Introduction

The Pudovik reaction is one of the most versatile pathways for the formation of carbon−phosphorus bonds (Scheme 1) and involves the addition of compounds containing a labile P−H bond with unsaturated systems (alkenes, alkynes, carbonyls, imines).[1,2]

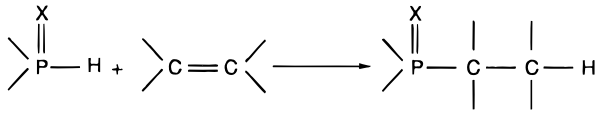
The products of the reaction find significant applications in a wide range of areas (industrial, biological, and chemical synthetic uses).[3] The Pudovik reaction can be considered as a "hybrid mechanism model" since it may proceed *via* an ionic and/or a radical mechanism, depending upon the structure of the unsaturated substrates and the phosphorus reagents and the experimental conditions. Although this reaction has been widely studied, a comparative study including various reagents and particularly different new activation methods has not been systematically done.

We now wish to report our studies of the Pudovik reaction with a series of alkenes and alkynes either being activated by electron-withdrawing substituents (C(O)OEt, C(O)Me, CN) or having nucleophilic character (Ph, alkyl), in the presence of various compounds containing a labile P−H bond such as diphenyl(thio)phosphine and diethyl phosphonate (Scheme 2).

Results and Discussion

These reactions were carried out in homogeneous or heterogeneous medium under various activation methods (heating, photochemical or ultrasonic irradiation, supported reactions in dry medium).

Scheme 1. Pudovik Reaction



X = lone pair, O or S

The choice of the various methods of activation was made according to the polar and/or radical character of the Pudovik reaction.

Method A: heterogeneous alkaline medium subjected to magnetic stirring and classical heating [Δ/KOH/H_2O/CH_3CN].

Method B: heterogeneous alkaline medium subjected to ultrasonic irradiation [))))/KOH/H_2O/CH_3CN].

Method C: basic solid support in dry medium [Al_2O_3/KOH].

Method D: homogeneous medium subjected to ultrasonic irradiation [))))].

Method E: homogeneous medium in the presence of a free radical initiator under classical heating [Δ/AIBN].

Method F: homogeneous medium in the presence of a free radical initiator subjected to ultrasonic irradiation [))))/AIBN].

Method G: homogeneous medium subjected to photochemical irradiation at 300 nm [*hν*].

The addition reactions of phosphorus reagents **1a**−**d** to ethylenic **2**−**4** and acetylenic **5**−**7** compounds were performed in either heterogeneous (methods A−C) or homogeneous medium (methods D-G). All the products obtained **2′**−**7′a**−**d**, **5″**−**7″a**−**d** and **8** (Scheme 2) were isolated, and their respective yields are reported in the Experimental Section. However, in order to rigourously compare the efficiency of the various activation methods, the initial yields were obtained by ^{31}P NMR analysis of the crude reaction mixtures prior to purification.

I. Influence of the nature of phosphorus reagents. (a) Diethyl Phosphonate (1a). The addition of diethyl phosphonate (**1a**) to α,*β*-unsaturated carbonyl compounds such as benzalacetone (**2**) in homogeneous

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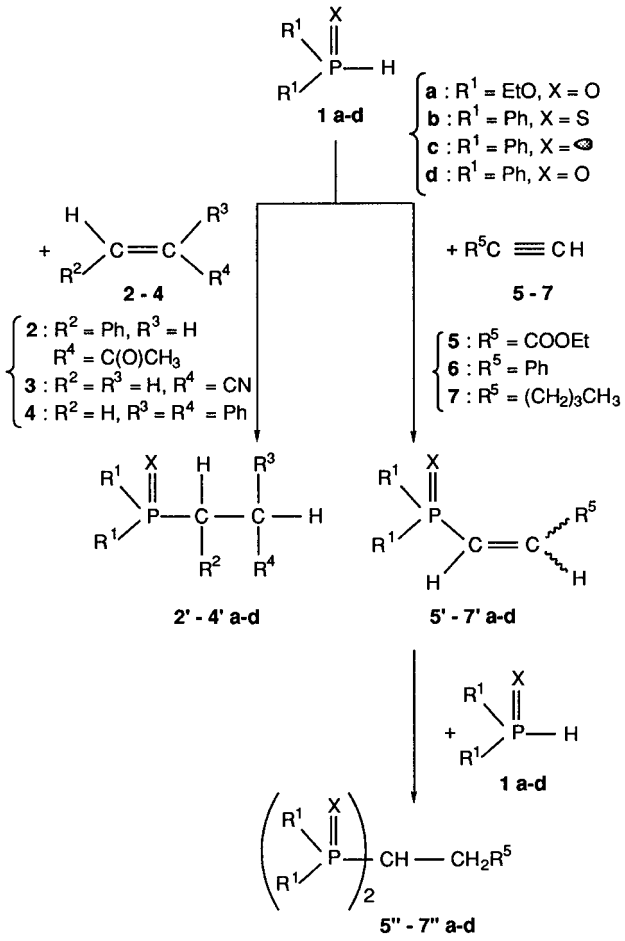
Scheme 2. General Scheme

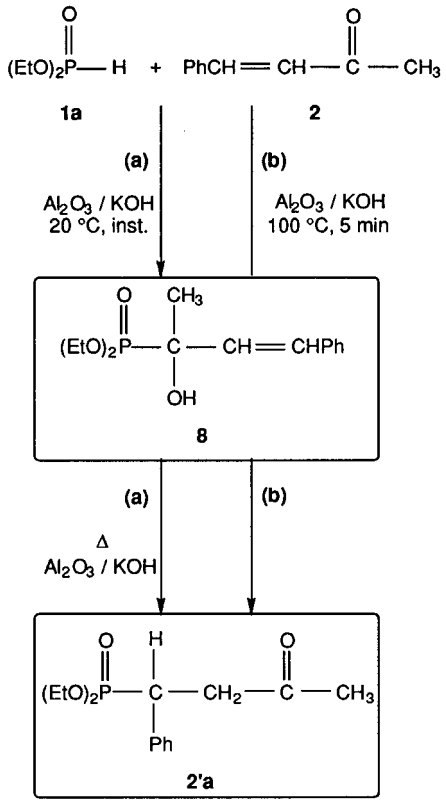


medium is not regioselective, since it occurs at either the C=O or the C=C double bond, giving rise to a mixture of α-hydroxy phosphonate **8** and β-keto phosphonate **2′a**.[4] A similar approach to the synthesis of α-hydroxy phosphonates involving the reaction of dialkyl phosphonates with nonactivated carbonyl reagents in dry medium was reported.[5] When the addition of diethyl phosphonate (**1a**) to benzalacetone (**2**) was performed on basic solid support in dry medium (method C), we observed that the regioselectivity and the ratio of the adducts were dependent on the reaction time and the temperature (Scheme 3).

Thus, the 1,2-adduct **8** was instantly obtained on Al_2O_3/KOH at 20 °C in 100% yield. The quantitative formation of the 1,4-adduct **2′a** required the use of Al_2O_3/KOH as the solid support at 100 °C for 5 min. The addition product **8** was the kinetic product and rearranged to the thermodynamic product **2′a**. This observation was verified by heating the α-hydroxy phosphonate **8** (in solution or directly adsorbed on solid support in dry medium); under these conditions, we obtained quantitatively the corresponding β-keto phosphonate **2′a**.

The hydrophosphonylation of ethyl propiolate (**5**) by diethyl phosphonate (**1a**) in homogeneous medium usually affords a mixture of single and double addition products in low yields.[6] In our case, this reaction proved to be regioselective on Al_2O_3/KOH in dry medium for 5

Scheme 3. Regioselective Synthesis of 8 (Pathway a) and 2′a [Pathways a (*Two-Steps*) and b (*One-Step*)]



min at 20 °C, giving rise to the double addition product **5″a** in 100% yield, regardless of the stoichiometry of the reagents.

The same method (method C) produced **3′a** after addition of diethyl phosphonate (**1a**) with acrylonitrile (**3**) in the yield of 81% whereas the yield did not exceed 33% by method B.

The addition of the diethyl phosphonate (**1a**) to the activated unsaturated compounds (benzalacetone (**2**), acrylonitrile (**3**), and ethyl propiolate (**5**)) occured in the presence of a basic catalyst (KOH) and particularly in the presence of this basic catalyst on solid support (method C). No reaction of diethyl phosphonate (**1a**) was observed with the nonactivated unsaturated substrates (diphenylethylene (**4**), phenylacetylene (**6**), and hexyne (**7**)) regardless of the method of activation (under our standard conditions) (Figure 1).

(b) Diphenylthiophosphine (1b). The diphenylthiophosphine (**1b**) underwent addition reactions with the activated systems such as benzalacetone (**2**), acrylonitrile (**3**), and ethyl propiolate (**5**) under anionic activation by three methods (A−C) (Figure 2).

The best yields of the reactions of diphenylthiophosphine (**1b**) with benzalacetone (**2**) and acrylonitrile (**3**) were obtained using method C (supported reactions in dry medium), affording the 1,4-adduct **2′b** and the product **3′b** in yield of 90% and 100% respectively, unlike the reaction with diethyl phosphonate (**1a**) and benzalacetone (**2**), no 1,2-adduct was detected.

However, with ethyl propiolate (**5**), method B gave the best results, giving rise to a mixture of the single addition product **5′b** and double addition product **5″b** in the overall yield of 80%. Diphenylthiophosphine (**1b**) also reacted with the activated substrates such as acrylonitrile (**3**) and ethyl propiolate (**5**) under photochemical

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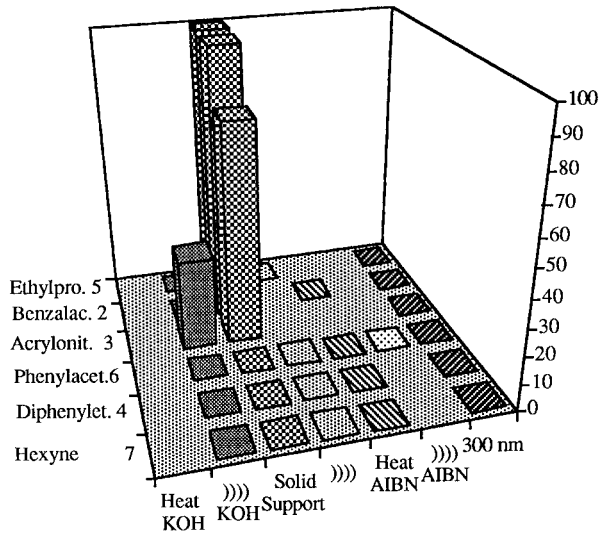

Figure 1. Reactivity of $(EtO)_2P(O)H$ (**1a**).

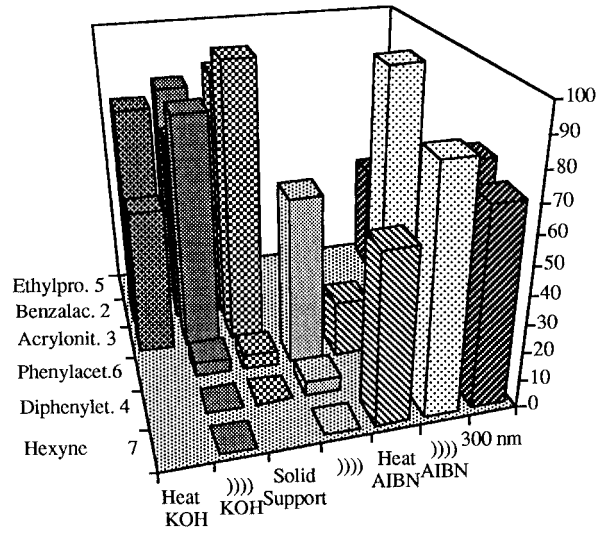

Figure 2. Reactivity of $Ph_2P(S)H$ (**1b**).

irradiation (method G) to give the adducts **3′b** and **5′b** in the same yield of 40%. In the case of the vinylic phosphine **5′b**, the *Z*/*E* ratio changed according to the method used: *Z*/*E* = 30/70 with method B and 55/45 with method G. It must also be noted that the double addition product **5″b** was only obtained in basic medium (*vide infra*).

Diphenylthiophosphine (**1b**) could not be reacted with the electron-rich unsaturated compounds (diphenylethylene (**4**), phenylacetylene (**6**), and hexyne (**7**)) under anionic activations but it underwent addition reactions under radical activations instead (Figure 2). The adducts **4′b**, **6′b**, and **7′b** were obtained under photochemical irradiation at 300 nm (method G) for 6−7 h in good yields. In the case of the phenylacetylene (**6**), the reaction led to the formation of the vinylic thiophosphine **6′b** in the yield of 60% under ultrasound irradiation in homogeneous medium for 1 h (method D). The yield of **6′b** under sonication was improved (>90%) by adding 3 equiv of AIBN (method F), whereas the same reaction under classical thermal method (method E) gave **6′b** in only 20%. It must also be noted that the photochemical reaction of diphenylthiophosphine (**1b**) with phenylacetylene (**6**) (method G) led to a photostationary equilibrium of the two isomers **6′b** (*Z*/*E* = 70/30). Interestingly, the

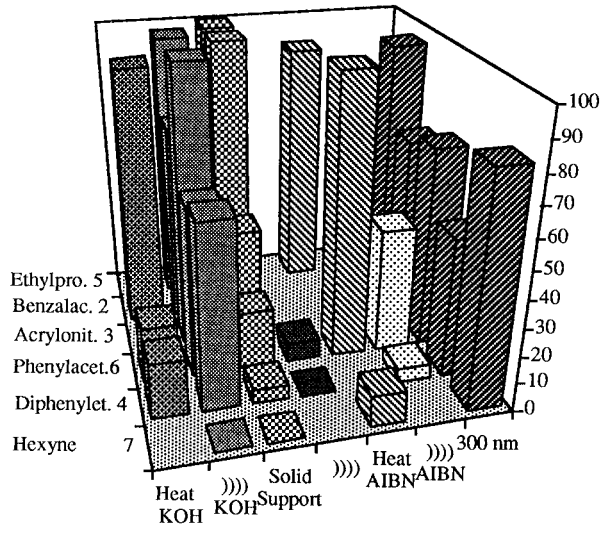

Figure 3. Reactivity of Ph_2PH (**1c**).

Scheme 4. Equilibrium between (Thio)phosphite ⇌ (Thio)phosphonate

reaction of **1b** with hexyne (**7**) did not take place under sonication in the absence of AIBN (method D) but afforded **7′b** in the yield of 85% with the *Z*/*E* ratio of 95/5 using method F [))))/AIBN]. The same reaction only afforded **7′b** in the yield of 60% by classical heating (method E) with the *Z*/*E* ratio of 75/25.

In summary, the diphenylthiophosphine (**1b**) presents a dual reactivity toward unsaturated systems since addition reactions occur under either radical- or base-catalyzed conditions, depending upon the nature of the multiple bond. A heterogeneous ionic process takes place with electron-deficient alkenes and alkynes (benzalacetone (**2**), acrylonitrile (**3**), and ethyl propiolate (**5**)), whereas addition reactions with electron-rich unsaturated substrates (diphenylethylene (**4**), phenylacetylene (**6**) and hexyne (**7**)) proceed *via* a radical mechanism in homogeneous medium.

(c) Diphenylphosphine (1c). Diphenylphosphine (**1c**) underwent addition reactions with almost all the unsaturated systems under base- or radical-catalyzed conditions (Figure 3).

However, the presence of the phosphorus electron lone pair makes diphenylphosphine (**1c**) particularly sensitive to oxidation reactions, especially under ultrasonic irradiation, with formation of the diphenylphosphine oxide (**1d**), which is much less reactive than diphenylphosphine (**1c**).

(d) Scale of the Reactivity. It is now well-established that the hydrophosphoryl compounds and their sulfur analogs exist as two tautomeric forms in equilibrium, but the equilibrium is almost completely shifted to the phosphoryl form[7] (Scheme 4).

However, both entities can react as nucleophiles in their (thio)phosphite and (thio)phosphonate forms in basic media. Their P−H acidities vary over a wide range,

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depending on the nature of substituents on the phosphorus atom. The thiophosphoryl derivatives are seen to be stronger acids than their corresponding oxygen analogs and their p*K* values are a few units lower (in DMSO):[8]

$$(EtO)_2P(O)H < Ph_2P(O)H < Ph_2P(S)H$$
$$[pK = 20.8] \quad [pK = 20.7] \quad [pK = 12.8]$$

Furthermore, the (thio)phosphoryl group is more electronegative than trivalent phosphorus, and $R_2P(X)H$ compounds are stronger acids than phosphines [$pK_{Ph_2PH} = 23.1$]. Their anions are ambident nucleophiles, $R_2PX^- \rightleftharpoons R_2P(X)^-$, but they rarely react at the oxygen or the sulfur atom. In the case of diphenyl(thio)phosphine, the "aryl effect" (the electron-acceptor effect of the phenyl groups) influences the partial negative charge on the phosphorus atom and stabilizes the anion. From the results described in Figures 1−3, an order of reactivity for the labile P−H reagents **1a**−**d** can be proposed:

$$(EtO)_2P(O)H < Ph_2P(O)H < Ph_2P(S)H < Ph_2PH$$

The order of the reagents in the scale of the reactivity corresponds to the one in the acidity scale except for diphenylphosphine, which is out of line dramatically. This probably reflects the difference in nucleophilicity between all the corresponding anions. The same trend of reactivity was observed with the corresponding radicals. Although, the abstraction of the labile hydrogen atom bonded to phosphorus is a similar process in both trivalent and tetrahedral compounds, it seems that the lower chain transfer constants for tetrahedral compounds reflect the lower stability of the (thio)phosphinyl radicals [$R_2P(X)^\bullet$] *vs* the phosphino radicals ($R_2P^\bullet$).[1a,9] Consequently, it can be assumed that secondary phosphines (e.g. Ph_2PH) are more reactive than hydro(thio)phosphoryl analogs. Furthermore, it has been shown that thiophosphinyl radicals (X = S) are more stable than phosphinyl radicals (X = O).[1b]

II. Influence of the Activation Methods. a) Anionic Activation. It is well-known that a wide variety of chemical reactions can be promoted in heterogeneous medium due to the presence of acidic and/or basic sites located on the surface of suitable solids such as alumina, clay, silica gel, and talc.[10] The advantages of such "dry media" reactions over their corresponding homogeneous counterparts are significant. The chemical transformations take place with better regiospecificity[11] and stereospecificity, the conditions are milder, and the isolation of products is easier. The anionic activation of the Pudovik reaction was carried out with potassium hydroxide supported on alumina in the absence of solvent ("dry medium process", method C), under sonication

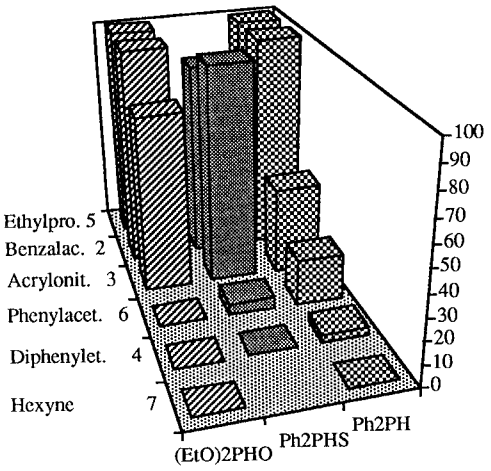

Figure 4. Comparative studies of the reactivity of the P−H bond upon basic solid support, the "dry medium process" (method C).

(method B), since ultrasound is known to be more effective in the case of heterogeneous reactions[12,13] and standard procedure (method A).

Among the methods used (methods A−C), the dry medium process can be considered as the best method for the anionic activation of the P−H labile bond toward alkenes and alkynes bearing strong electron-withdrawing substituents. Figure 4 correlates the efficiency of the method C and the nature of the unsaturated substrate.

Several solid mineral supports (neutral or activated basic alumina and lamellar structures such as talc) were tested. Commercial basic alumina was not efficient compared to the more basic potassium hydroxide impregnated upon alumina. The use of KOH supported on alumina rendered the Pudovik reaction fast and regiospecifically. It also made the workup easier: the reagents were adsorbed on the solid support, the reaction occurred almost instantly at room temperature and a simple extraction using the appropriate solvent followed by filtration directly afforded the addition products. It is important to note that the amount of water adsorbed is critical since the completion and the selectivity of the reaction heavily depended on the degree of dryness of the basic supports.[14] We finalized the cyanoethylation reaction of the phosphine PH_3—well-known in homogeneous medium[15] or in heterogeneous medium (liquid−liquid)[13]—in heterogeneous "gas/solid" medium. We studied the influence of the varying degrees of dryness of solid support (Al_2O_3/KOH in the ratio of 2.5/1), upon the progress of the reaction (Scheme 5).

The thermogravimetric analysis of the solid support obtained as a fine powder after evaporation for 1.5 h under reduced pressure (15−20 mm) indicated the presence of 4% (Figure 5a) of physically adsorbed water whereas the same analysis of another support obtained as a granular powder (30 min under 15−20 mm) revealed 21% of water (Figure 5b). Our experimental results

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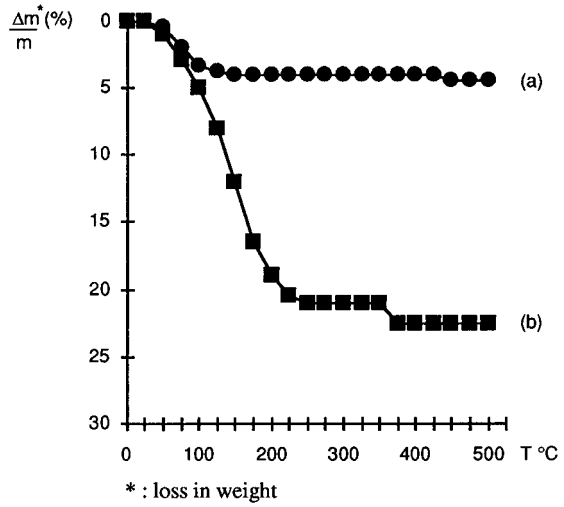


Figure 5. Thermogravimetric analysis of Al_2O_3/KOH (2.5/1) solid support after evaporation [(a) 1.5 h and (b) 30 min] under reduced pressure (15−20 mmHg).

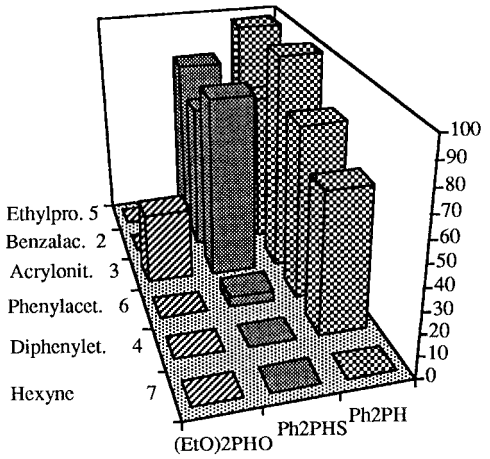
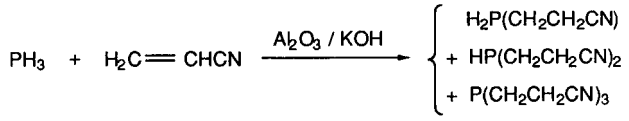


Figure 6. Comparative studies of the reactivity of the P−H bond upon sonication in basic heterogeneous medium (method B).

Scheme 5. Cyanoethylation Reaction of Phosphine PH_3



showed that the reaction only occurred with the solid support containing a lesser amount of water (4%).

The sonication of a heterogeneous basic medium (method B) enhanced the addition rate and improved the yield with respect to the standard procedure (method A). Figure 6 shows the scale of the reactivity of phosphorus compounds using method B.

Furthermore, method B constituted an efficient method for the preparation of the double addition product in the reaction of diphenylphosphine (**1c**) with phenylacetylene (**6**): the oxidized double addition adduct **6″d** was obtained in a yield of 40% along side with the corresponding single addition product **6′c** (16%) and its oxidized analog **6′d** (12%). For the same reaction, the dry medium method afforded **6″d** in only 16% yield.

(b) Radical Activation. Free radical addition reactions were very efficient when the double or triple bond

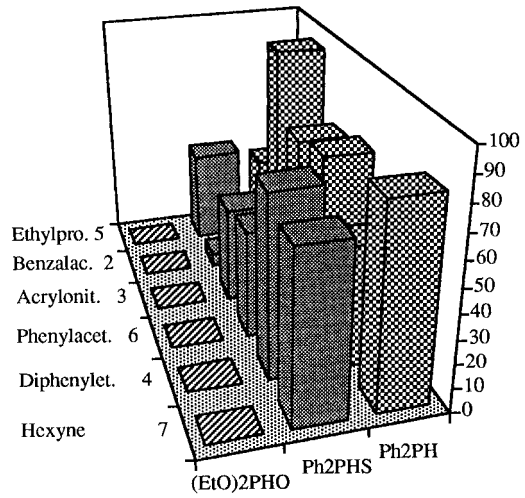


Figure 7. Comparative studies of the reactivity of the P−H bond under photochemical irradiation at 300 nm (method G).

of unsaturated compounds was not strongly polarized (Figure 7).

It is known that ultrasound can promote a single electron transfer and favor the radical mechanism.[16] Method D [))))] and method F [))))/AIBN] allowed us to test this observation with respect to classical methods for the generation of radicals such as methods E [Δ/AIBN] and G [*hν*].

From these results (Figures 1−3), the photochemical activation (method G) was very efficient for the radical addition of diphenyl(thio)phosphine (**1b**,**c**) to electron-rich alkenes and alkynes (Figure 7). However, the reaction required a long irradiation time, bringing about the isomerization of the corresponding vinylic (thio)-phosphine adducts. No reaction took place with diethyl phosphonate (**1a**), regardless of the unsaturated substrates **2**−**7** and the radical activation methods (methods D-G). This observation may appear paradoxical in the light of the known examples of free radical reactivity of diethyl phosphonate (**1a**)[2,17] described by Pudovik, but our standard chosen methods were less drastic. Furthermore, the reaction mechanism depends on the nature of the unsaturated substrates since, in our recent studies,[18] we have shown that the addition of diethyl phosphonate (**1a**) with imines was improved by ultrasonic activation. The radical mechanism of this reaction was confirm by EPR[19] while the addition of the same compound **1a** with aldehydes[20] was anionic.

The cavitational effects of ultrasonic irradiation depend on many physical parameters (viscosity, boiling point, vapor pressure, macroscopic temperature, etc.).[21,22] It seems likely that the sonochemical effects for the studied reaction mixtures (**1a** with **2**−**7**) are not sufficiently effective to initiate the addition reactions. It was de-

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scribed that the use of high frequency of ultrasound for radical reactions[23] or the simultaneous action of two acoustic vibration frequencies[21] is much more effective than the action of each frequency separately. Therefore, we used an ultrasonic bath at 536 kHz or the coupling of the two frequencies (20 and 536 kHz) for radical generation. However, both methods offered no improvement of yields. This nonreactivity of diethyl phosphonate (**1a**) with alkenes and alkynes under radical activation could be due to the nature of the couple "P−H reagent/unsaturated substrate" and consequently to the addition reaction rate of the phosphinyl radical [$(EtO)_2P(O)^{\bullet}$] with unsaturated substrate. Actually, the reaction rate is higher for the imines[18] than for our unsaturated substrates **2**−**7**.

The addition reaction of diphenylthiophosphine (**1b**) with hexyne did not take place under sonication and the presence of a radical initiator is required. In contrast, the reaction of diphenylthiophosphine (**1b**) with phenylacetylene (**6**) can occur under sonication in toluene without AIBN. The influence of the nature of solvent upon the latter reaction is observed: although the dichloroethane is known to generate radicals under ultrasonic irradiation,[24] the presence of this solvent rendered the sonication ineffective in our case and the use of toluene became necessary. Consequently, the chemical effects of ultrasound activation in homogeneous medium remain uncertain and unpredictable as a function of the chemical and physical properties of the reaction mixture. However, the sonication in homogeneous medium and in the presence of a radical initiator can become an appropriated method *versus* the photochemical activation for the synthesis of vinylic phosphorus derivatives since the reaction time is reduced to 1 h and the stereoselectivity of the reaction reaches much to 95% in favor of the *Z* isomers.

Under the conditions described in this work, the P−H reagents regioselectively add to unsaturated compounds by nucleophilic or free-radical mechanism. In the presence of free-radical initiators or under photochemical or ultrasound irradiation in homogeneous medium, the reagents **1a**−**d** add to double and triple bonds by a free-radical mechanism and the orientation is anti-Markovnikov. In basic medium, the addition occurs by nucleophilic attack of phosphorus anions to olefins or alkynes by a Michael type mechanism and the orientation is also anti-Markovnikov, the nucleophile going to the least-substituted carbon and the electrophile going to the most-substituted position. In fact, the orientation cannot be used as a diagnostic tool to indicate which mechanism is operating.

Conclusion

It appears in the literature that the differences of the Pudovik reaction mechanisms depend upon the nature of the unsaturated substrates. Although the comparison between the different activation methods used must be made wisely because each method is not optimized for each reaction in order to keep the standard conditions, our results show that the phosphorus atom environment allows us to define more precisely the reactional domains.

Radical activation is mainly favorable to the addition reaction between unsaturated systems having a nucleophilic character with diphenylphosphine or diphenylthiophosphine. When the phosphorus atom bears an oxygen, the radical addition reaction in our particular experimental conditions (less drastic than the literature conditions) does not occur with ethylenic or acetylenic compounds. Photoactivation is the most efficient method, but the reaction time is long and entails often an isomerization of the vinyl(thio)phosphines obtained. Ultrasound-induced radical reactions in homogeneous medium is mostly unpredictable because several parameters have to be taken into account such as the nature of the reagents, the solvent's viscosity and boiling point, and the temperature, but it can be superior to photochemistry since the reaction time is shorter and only the cis configuration is obtained by this method.

When an *anionic activation* is used—particularly when the unsaturated system is activated by an electron-withdrawing substituent—the dry media process on basic solid support is the best method. The contribution of ultrasound to ionic reactions in heterogeneous medium (liquid/liquid) is mainly due to the mechanical effects (homogenization, emulsification). Under these conditions, the reaction's rate, selectivity, and yield are increased in relation to classical process.

In conclusion, this comparative study of the different activation methods allowed us to define the scope of application depending upon the nature of the unsaturated substrate (activated or not), the nature of the organophosphorus compound (phosphorus atom oxidized or not), and the experimental conditions:

When the phosphorus atom bears an oxygen or sulfur atom, the domains of the reactivity are well-separated. When the substrate used is an unsaturated system having a nucleophilic character, the mechanism is preferentially radical. When the unsaturated compound contains an electron-withdrawing substituent, the main mechanism is ionic. Then, we notice that the mechanism may be either radical or ionic, depending upon the nature of the substrate, *whatever* the experimental method used.

When the phosphorus atom is not oxidized (in the case of the diphenylphosphine), the fields of the radical/ionic mechanisms are not distinguishable; there is a duality of the mechanisms and the coexistence of these two processes brings about a competition which *depends* on the experimental conditions.

Experimental Section

General Comments. The spectra were recorded using the following instruments: IR spectra, Beckman IR10 or Perkin-Elmer 225; ^1H, ^{13}C, and ^{31}P spectra, Brucker AC80 or 250WM; and mass spectra in the electron impact mode, Varian Mat 311A. Column chromatographic separations were executed at normal pressure using Merck silica 60F (70−230 mesh). Melting points were measured in open glass capillaries with a Büchi-Tottoli apparatus. Elemental analyses were performed by the Microanalytical Service Laboratory of the "Ecole Nationale Superieure de Chimie" of Toulouse, France. UV irradiation (300 nm) was performed on Rayonet RPR100 apparatus. The ultrasound generator was a 13 mm probe fitted to a Bioblock Vibracell 600W (20 kHz) generator dipped into the solution.

Diethyl phosphonate (**1a**), benzalacetone (**2**), acrylonitrile (**3**), 1-hexyne (**7**) (Aldrich), diphenylphosphine (**1c**), 1,1-diphenylethylene (**4**), ethyl propiolate (**5**) (Fluka) and phenylacetylene (**6**) (Lancaster) were used as received without prior purification. Solid supports were purchased from Janssen (Al_2O_3, 50−200 μm).

When reactions were performed *via* methods A−D, materials were obtained from commercial suppliers and used without

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further purification. For methods E−G, reactions were carried out under an argon atmosphere with dry distilled solvents under anhydrous conditions.

General Procedures. Methods A [Δ/KOH] and B [))))/KOH]. To a solution of phosphorus compounds **1a**−**d** (0.73 mmol) in acetonitrile (3 mL) was added potassium hydroxide (1.24 mmol) in distilled H_2O (2.42 mmol). An unsaturated system **2**−**7** (0.73 mmol, except 2.9 mmol for acrylonitrile (**3**)) was added to the solution. The mixture was stirred at 70 °C (or sonicated at 70 °C) for 1 h.

Method C [Al_2O_3/KOH]. A 1:5 ratio of phosphorus reactant/support and a 1:1.7 molar ratio of phosphorus reactant/base was used. The following general procedure was used: potassium hydroxide supported on alumina was added to a solution of phosphorus compounds **1a**−**d** (0.73 mmol) and an unsaturated substrate **2**−**7** (0.73 mmol, except 2.9 mmol for acrylonitrile (**3**)) dissolved in a minimum of CH_2Cl_2 (3−4 mL) at room temperature. The solvent was evaporated under reduced pressure during 1.5 at 15−20 mmHg and the adduct was extracted by an appropriate solvent (specified for each product in the description of the purification).

Methods D [Δ/AIBN], E [))))] and F [))))/AIBN]. To a solution of an unsaturated compound **2**−**7** (0.73 mmol, except 2.9 mmol for acrylonitrile (**3**)) in distilled solvent (4 mL) placed in air-dried material was added phosphorus reagents **1a**−**d** (0.73 mmol). For the methods D and F, AIBN (2.9 mmol) was added to this mixture. The resulting solution was stirred and heated or sonicated at 70 °C.

Method G [*hν*/300 nm]. A phosphorus compound **1a**−**d** was dissolved in 0.3 mL of deuteriated solvent and was added to an unsaturated system **2**−**7** (0.73 mmol, except 2.9 mmol for acrylonitrile (**3**)). This solution was irradiated at 300 nm (the reaction time and the nature of the solvent are specified for each product in the description of the purification).

Diphenylphosphine Sulfide (1b). To a solution of diphenylphosphine (**1c**) (1 g, 5.4 mmol) in distilled toluene (10 mL) was added S_8 (173 mg, 5.4 mmol) in air-dried material. This solution was stirred and heated at 80 °C for 2.5 h. The solvent was removed and the crude product **1b** was recrystallized from CH_3CN to yield 1.05 g of white solid (90%): mp 98−99 °C (from CH_3CN);[25] ^{31}P NMR (32.44 MHz, C_6D_6) δ 20.9 (d, $^1J_{PH}$ = 465 Hz); ^{1}H NMR (80.13 MHz, C_6D_6) δ 7.72 (d, $^1J_{HP}$ = 465 Hz, 1H), 7.70 (m, 10H); IR (KBr, cm^{-1}) 3060 (Ph), 695 (P═S); MS (EI) *m*/*z* 219 (M + 1)$^{+\bullet}$.

***O,O′*-Diethyl (3-Oxo-1-phenylbutyl)phosphonate (2′a).** This compound was obtained by method C [Al_2O_3/KOH]. The supported reagents were heated at 100 °C for 5 min. The crude product was obtained after extraction with acetone and was chromatographed on silica (eluent: *n*-hexane/AcOEt, 1:9), affording the expected product **2′a** (65%) as a yellow oil:[4] R_f 0.28 (*n*-hexane/AcOEt, 1:9); ^{31}P NMR (32.44 MHz, C_6D_6) δ 27.6 (m); ^{1}H NMR (80.13 MHz, C_6D_6) δ 7.53−7.04 (m, 5H), 3.92 (q, $^3J_{HH}$ = 7.3 Hz, 2H), 3.84 (q, $^3J_{HH}$ = 6.4 Hz, 2H), 3.80−3.58 (m, 1H), 3.18−2.81 (m, 2H), 1.55 (s, 3H), 1.01 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.82 (t, $^3J_{HH}$ = 6.4 Hz, 3H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 203.52 (d, $^3J_{CP}$ = 14.0 Hz), 137.20 (d, $^2J_{CP}$ = 6.7 Hz), 129.77 (d, $^2J_{CP}$ = 2.5 Hz), 128.61 (s), 127.32 (s), 62.67 (d, $^2J_{CP}$ = 6.7 Hz), 61.72 (d, $^2J_{CP}$ = 7.1 Hz), 44.07 (d, $^2J_{CP}$ = 1.7 Hz), 39.51 (d, $^1J_{CP}$ = 139.7 Hz), 16.47 (d, $^3J_{CP}$ = 5.8 Hz), 16.28 (d, $^3J_{CP}$ = 5.5 Hz); IR (C_6D_6, cm^{-1}) 1738 (C═O), 1252 (P═O); MS (EI) *m*/*z* 284 (M)$^{+\bullet}$, 241 (M − C(O)CH_3)$^+$.

O,O′-Diethyl (2-Cyanoethyl)phosphonate (3′a). This adduct was obtained by methods B [))))/KOH] and C [Al_2O_3/KOH].

Purification after Method B. The organic solvent was separated from the aqueous phase and *n*-hexane was added to the organic phase. The crude product **3′a** was obtained as a yellow oil. This oil was separated from the solvents and was dried under vacuum to yield 12% of the expected adduct **3′a**.

Purification after Method C. The solid support was extracted with MeOH and the filtrate was purified on chromatography on silica (eluent: MeOH) to yield 55% of the adduct **3′a** as a yellow oil:[26] R_f 0.60 (MeOH); ^{31}P NMR (32.44 MHz, $CDCl_3$) δ 25.8 (m); ^{1}H NMR (80.13 MHz, $CDCl_3$) δ 4.13 (qd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 8.3 Hz, 4H), 2.79−2.44 (m, 2H), 2.26−1.85 (m, 2H), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 6H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 118.77 (d, $^3J_{CP}$ = 15.1 Hz), 62.51 (d, $^2J_{CP}$ = 6.1 Hz), 21.84 (d, $^1J_{CP}$ = 144.9 Hz), 16.37 (d, $^3J_{CP}$ = 5.8 Hz), 11.27 (d, $^2J_{CP}$ = 4.1 Hz); IR ($CDCl_3$, cm^{-1}) 2244 (CN), 1245 (P═O); MS (EI) *m*/*z* 192 (M + 1)$^{+\bullet}$, 136 [(M − CH_2CH_2CN − 1)]$^+$.

O,O′-Diethyl (1-Hydroxy-1-methyl-3-phenyl-2-propenyl)phosphonate (8). Method C [Al_2O_3/KOH] was used. Products were extracted with acetone and **8** was purified by chromatography on silica (eluent: *n*-hexane/AcOEt, 1:9) to yield 63%: yellow oil;[4] R_f 0.25 (*n*-hexane/AcOEt, 1:9); ^{31}P NMR (32.44 MHz, C_6D_6) δ 23.8 (m); ^{1}H NMR (250.13 MHz, C_6D_6) δ 7.37−7.35 (m, 2H), 7.20 (d, $^3J_{HH}$ = 4.5 Hz, 1H), 7.16−7.01 (m, 3H), 6.66 (dd, $^3J_{HH}$ = 4.5 Hz,$^3J_{HP}$ = 15.9 Hz, 1 H), 6.37 (s, 1H), 4.18−4.04 (m, 4H), 1.84 (d, $^3J_{HP}$ = 15.8 Hz, 3H), 1.08 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 1.05 (t, $^3J_{HH}$ = 7.3 Hz, 3H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 137.65 (d, $^4J_{CP}$ = 3.0 Hz), 131.08 (s), 130.10 (d, $^2J_{CP}$ = 10.5 Hz), 128.88−127.01 (m), 73.07 (d, $^1J_{CP}$ = 161.3 Hz), 63.56 (d, $^2J_{CP}$ = 7.4 Hz), 62.92 (d, $^2J_{CP}$ = 7.8 Hz), 24.45 (d, $^2J_{CP}$ = 2.3 Hz), 16.62 (s), 16.53 (s); IR (C_6D_6, cm^{-1}) 3257 (OH), 1603 (C═C), 1240 (P═O); MS (EI) *m*/*z* 284 (M)$^{+\bullet}$, 103 (CH═CHPh)$^+$, 29 (CH_3CH_2)$^+$. Anal. Calcd for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.45. Found: C, 59.01; H, 7.38.

3,3-Bis(diethoxyphosphinyl)prop-2-anoic Acid Ethyl Ester (5″a). Method C [Al_2O_3/KOH] was used to obtain **5″a**. The solid support was extracted with acetone and **5″a** was purified by chromatography (SiO_2; eluent:CH_2Cl_2/*n*-hexane, 1:9) to give 60% of **5″a** as a yellow oil:[6] R_f 0.26 (CH_2Cl_2/*n*-hexane, 1:9); ^{31}P NMR (32.44 MHz, C_6D_6) δ 21.1 (m); ^{1}H NMR (200.13 MHz, C_6D_6) δ 4.11 (qd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HP}$ = 9.0 Hz, 4H), 4.07 (qd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HP}$ = 9.0 Hz, 4H), 3.94 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 3.44 (tt, $^3J_{HH}$ = 6.0 Hz, $^2J_{HP}$ = 24.0 Hz, 1H), 3.07 (dt, $^3J_{HH}$ = 6.0 Hz, $^2J_{HP}$ = 16.0 Hz, 2H), 1.07 (t, $^3J_{HH}$ = 8.0 Hz, 6H), 1.06 (t, $^3J_{HH}$ = 8.0 Hz, 6H), 0.93 (t, $^3J_{HH}$ = 8.0 Hz, 3H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 171.01 (s), 62.88 (d, $^2J_{CP}$ = 6.3 Hz), 62.61 (d, $^2J_{CP}$ = 6.3 Hz), 61.03 (s), 33.91 (t, $^1J_{CP}$ = 135.2 Hz), 31.40 (t, $^2J_{CP}$ = 4.4 Hz), 16.04 (d, $^3J_{CP}$ = 3.8 Hz), 16.03 (d, $^3J_{CP}$ = 3.8 Hz), 14.11 (s); IR (C_6D_6, cm^{-1}) 1738 (C═O), 1252 (P═O); MS (EI) *m*/*z* 375 (M + 1)$^{+\bullet}$, 301 [(M − CO_2Et)]$^{+\bullet}$.

(3-Oxo-1-phenylbutyl)diphenylphosphine sulfide (2′b) was obtained by methods A [Δ/KOH], B [))))/KOH], and C [Al_2O_3/KOH].

Purification after Methods A and B. The organic phase was separated from the aqueous phase and acetonitrile was removed under vacuum. To this mixture was added H_2O. The crude expected product was precipitated. The white solid was separated from the supernatent and recrystallized at low temperature from EtOH to yield 47% (method A) and 40% (method B) of **2′b** as a white solid.

Purification after Method C. The solid support was extracted with EtOH. This solution was concentrated and placed at low temperature. The product **2′b** was obtained (64%) as a white solid: mp 149−151 °C (from EtOH);[27] ^{31}P NMR (32.44 MHz, C_6D_6) δ 50.1 (m); ^{1}H NMR (250.13 MHz, C_6D_6) δ 8.28−6.76 (m, 15 H), 4.83 (td, $^3J_{HH}$ = 2.7 Hz, $^2J_{HP}$ ∼ $^3J_{HH}$ = 10.0 Hz, 1H), 3.30 (ddd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HP}$ = 5.4 Hz, $^2J_{HH}$ = 18.2 Hz, 1H), 2.80 (ddd, $^3J_{HH}$ = 2.7 Hz, $^3J_{HP}$ = 13.0 Hz, $^2J_{HH}$ = 18.2 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 204.09 (d, $^3J_{CP}$ = 14 Hz), 136.21 (s), 133.10−127.55 (m), 44.67 (d, $^2J_{CP}$ = 4 Hz), 41.44 (d, $^1J_{CP}$ = 53 Hz), 29.99 (s); IR (KBr, cm^{-1}) 3052 (Ph), 1710 (C═O), 694 (P═S); MS (EI) *m*/*z* 364 (M)$^{+\bullet}$, 217 (Ph_2P═S)$^+$, 43 (CH_3C═O)$^+$.

(2-Cyanoethyl)diphenylphosphine Sulfide (3′b). Methods A [Δ/KOH], B [))))/KOH], C [Al_2O_3/KOH], and G [*hν*/300nm] were used for the synthesis of **3′b**.

Purification after Methods A and B. The organic phase was separated from aqueous phase, removed, and added to toluene. The brown precipitate was filtered off and taken up in EtOH. This mixture was placed at low temperature and **3′b** was obtained (47% with method A and 76% with method B) as white needles.

Purification after Method C. Products were extracted with acetone and the solvent was removed under vacuum.

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Compound **3′b** was obtained after recrystallization from EtOH at low temperature (82%) as white needles.

Purification after Method G. Deuteriated benzene was removed after 6 h under irradiation and was added to petroleum ether. The adduct **3′b** was precipitated, separated from supernatent, and recrystallized from EtOH with a yield of 35%: mp 128−129 °C (from EtOH);[28] ^{31}P NMR (32.44 MHz, $CDCl_3$) δ 41.1 (m); ^{1}H NMR (80.13 MHz, $CDCl_3$) δ 7.96−7.67 (m, 4H), 7.54−7.41 (m, 6H), 2.81−2.62 (m, 4H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 132.28 (d, $^4J_{CP}$ = 2.8 Hz), 131.09 (d, $^2J_{CP}$ = 10.5 Hz), 130.91 (d, $^1J_{CP}$ = 82.4 Hz), 129.05 (d, $^3J_{CP}$ = 12.5 Hz), 118.60 (d, $^3J_{CP}$ = 20.0 Hz), 28.89 (d, $^1J_{CP}$ = 56.5 Hz), 11.29 (s); IR (KBr, cm^{-1}) 3060 (Ph), 2239 (CN), 1437 (CH_2CN), 697 (P═S); MS (EI) *m*/*z* 271 (M)$^{+\bullet}$, 218 [(M − CH_2CH_2CN) + 1]$^{+\bullet}$. Anal. Calcd for $C_{15}H_{14}NPS$: C, 66.40; H, 5.20; N, 5.16. Found: C, 66.15; H, 5.18; N, 5.07.

(2,2-Diphenylethyl)diphenylphosphine Sulfide (4′b). This synthesis was realized by method G [*h*ν/300 nm] in deuteriated benzene. The solvent was removed under vacuum. Compound **4′b** was recrystallized from MeOH at low temperature and obtained with a yield of 55% as a white solid: mp 154−155 °C (from MeOH); ^{31}P NMR (32.44 MHz, C_6D_6) δ 40.5 (m); ^{1}H NMR (80.13 MHz, C_6D_6) δ 7.75−7.50 (m, 4H), 7.18−6.79 (m, 16H), 5.23 (td, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.9 Hz, 1H), 3.05 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HP}$ = 11.3 Hz, 2H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 144.1 (d, $^3J_{CP}$ = 8.3 Hz), 134.1 (d, $^1J_{CP}$ = 80.3 Hz), 131.54−126.51 (m), 45.6 (s), 38.8 (d, $^1J_{CP}$ = 55.2 Hz); IR (KBr, cm^{-1}) 3051 (Ph), 694 (P═S); MS (EI) *m*/*z* 398 (M)$^{+\bullet}$, 218 [(M − CH_2CHPh_2) + 1]$^{+\bullet}$, 181 (Ph_2CHCH_2)$^+$, 140 (PhP═S)$^{+\bullet}$. Anal. Calcd for $C_{26}H_{23}PS$: C, 78.36; H, 5.82. Found: C, 78.17; H, 5.78.

Diphenyl-*cis*-*β*-styrylphosphine Sulfide (6′b). Adduct **6′b** was obtained by methods E [)))))], F [)))))/AIBN], and G [*h*ν, 300 nm, 6 h]. After the synthesis by each method, the solvent was evaporated. Hexane was added and the crude product **6′b** was precipitated. The product was purified by recrystallization from EtOH after methods E (40%) and G (30%) and by chromatography (SiO_2; eluent: *n*-hexane/AcOEt, 99:1) after synthesis by method F (65%). Compound **6′b** was obtained as a white solid: R_f 0.30 (*n*-hexane/AcOEt, 99:1); mp = 108−109 °C (from EtOH);[29] ^{31}P NMR (32.44 MHz, C_6D_6) δ 29 (m); ^{1}H NMR (250.13 MHz, C_6D_6) δ 7.99−7.89 (m, 3H), 7.65−7.60 (m, 2H), 7.16−7.15 (m, 2H), 7.03 (d, $^3J_{HH}$ = 13.6 Hz, 1H), 7.05−6.75 (m, 8H), 6.11 (dd, $^2J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 13.6 Hz, 1 H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 146.00 (d, $^2J_{CP}$ = 2.5 Hz), 136.18 (s), 134.49 (d, $^1J_{CP}$ = 85.1 Hz), 131.63−127.69 (m), 124.08 (d, $^1J_{CP}$ = 81.5 Hz); IR (KBr, cm^{-1}) 3051 (Ph), 1595 (C═C), 694 (P═S); MS (EI) *m*/*z* 320 (M)$^{+\bullet}$, 218 [(M − PhCH═CH) + 1]$^{+\bullet}$, 78 (Ph + 1)$^{+\bullet}$.

(1-Hexenyl)diphenylphosphine Sulfide (7′b). The mixture was irradiated for 7 h under 300 nm light (method G). The toluene was removed and **7′b** was obtained as a white solid after recrystallization in EtOH at low temperature with a yield of 34%: ^{31}P NMR (32.44 MHz, $CDCl_3$) δ −14.1 (m) (cis isomer), −31.7 (m) (trans isomer); ^{1}H NMR (250.13 MHz, $CDCl_3$) (cis isomer) δ 8.01−7.52 (m, 10 H), 6.57 (tdd, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 42.9 Hz, 1H), 6.32 (tdd, $^3J_{HH}$ = 12.4 Hz, $^4J_{HH}$ = 1.52 Hz, $^2J_{HP}$ = 23.6 Hz, 1H), 2.27 (m, 2H), 1.23 (m, 4H), 0.78 (t, $^3J_{HH}$ = 7.9 Hz, 3H); ^{13}C NMR (62.90 MHz, $CDCl_3$) (cis isomer) δ 153.50 (s), 134.02 (d, $^1J_{CP}$ = 83.2 Hz), 131.25 (d, $^3J_{CP}$ = 13.1 Hz), 128.03 (d, $^3J_{CP}$ = 12.3 Hz), 123.06 (d, $^1J_{CP}$ = 84.4 Hz), 30.67 (d, $^3J_{CP}$ = 9.5 Hz), 30.46 (s), 22.22 (s), 13.61 (s); IR (C_6D_6, cm^{-1}) (cis isomer) 3054 (Ph), 1434 (C═C); MS (EI) *m*/*z* 300 (M)$^{+\bullet}$, 271 (M − CH_2CH_3)$^+$, 108 (PhP)$^{+\bullet}$. Anal. Calcd for $C_{18}H_{21}PS$: C, 71.97; H, 7.05. Found: C, 71.55; H, 7.05.

(2-Cyanoethyl)diphenylphosphine (3′c). Methods B [)))))/KOH] and G [*h*ν/300nm] was used for the synthesis of **3′c**.

Purification after Method B. The organic liquid phase was separated from the aqueous phase and the solvent was removed under vacuum. The crude product **3′c** precipitated after addition of *n*-hexane. This solution was concentrated and placed at low temperature to yield 76% of **3′c**.

Purification after Method G. The solvent was evaporated and *n*-hexane was added. After some hours at low temperature, 61% of **3′c** was obtained as a white solid: mp 43−45 °C (from *n*-hexane); ^{31}P NMR (32.44 MHz, C_6D_6) δ −16.9 (m); ^{1}H NMR (250.13 MHz, C_6D_6) δ 7.18−7.01 (m, 10H), 1.75−1.59 (m, 4H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 137.38 (d, $^1J_{CP}$ = 13.5 Hz), 132.97 (d, $^2J_{CP}$ = 19.2 Hz), 129.23 (s), 128.93 (d, $^3J_{CP}$ = 6.9 Hz), 94.90 (d, $^3J_{CP}$ = 18.1 Hz), 24.19 (d, $^2J_{CP}$ = 15.7 Hz), 13.73 (d, $^1J_{CP}$ = 24.1 Hz); IR (KBr, cm^{-1}) 3067 (Ph), 2246 (CN), 1429 (CH_2CN); MS (EI) *m*/*z* 239 (M)$^{+\bullet}$. Anal. Calcd for $C_{15}H_{14}NP$: C, 75.30; H, 5.90; N, 5.85. Found: C, 74.70; H, 6.00; N, 5.62.

(2,2-Diphenylethyl)diphenylphosphine (4′c). This compound was synthetized by method G [*h*ν/300nm] after 26.5 h. The product **4′c** was purified by chromatography (SiO_2; eluent: CH_2Cl_2/AcOEt, 7:3) to give 23% of a colorless oil:[27] R_f 0.90 (CH_2Cl_2/AcOEt, 7:3); ^{31}P NMR (32.44 MHz, C_6D_6) δ −20.9 (m); ^{1}H NMR (80.13 MHz, C_6D_6) δ 7.45−7.28 (m, 4H), 7.15−6.90 (m, 16H), 4.06 (td, $^2J_{HP} \sim {}^3J_{HH}$ = 7.9 Hz, 1H), 2.81 (d, $^3J_{HH}$ = 7.9 Hz, 2H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 145.33 (d, $^1J_{CP}$ = 9.0 Hz), 128.80−122.21 (m), 48.73 (d, $^2J_{CP}$ = 15.7 Hz), 114.36 (s), 36.38 (d, $^1J_{CP}$ = 14.8 Hz); IR (C_6D_6, cm^{-1}) 3057 (Ph); MS (EI) *m*/*z* 366 (M)$^{+\bullet}$, 199 (Ph_2PCH_2)$^+$, 181 [(M − Ph_2P)+1]$^+$, 77 (Ph)$^+$.

Ethyl 3-(Diphenylphosphino)prop-2-enoate (5′c). Method B [)))))/KOH] was used in this synthesis. The organic phase was separated from the aqueous phase and was extracted with *n*-hexane. The acetonitrile phase contained compound **5″d** (see description of **5″d**) and the hexane phase compound **5′c**. The *n*-hexane solution was concentrated and placed at low temperature. A precipitate formed. The supernatent was separated and the solvent was evaporated to give 40% of **5′c** as a white solid: ^{31}P NMR (32.44 MHz, C_6D_6) δ −11.2 (m) (cis isomer), −13.2 (m) (trans isomer); ^{1}H NMR (80.13 MHz, C_6D_6) (ratio cis/trans, 50:50) δ 7.76 (dd, $^3J_{HH}$ = 16.8 Hz, $^2J_{HP}$ = 4.0 Hz, 1H), 7.10 (dd, $^3J_{HH}$ = 12.3 Hz, $^2J_{HP}$ = 1.5 Hz, 1H), 6.51 (dd, $^3J_{HH}$ = 12.3 Hz, $^3J_{HP}$ = 15.4 Hz, 1H), 5.83 (dd, $^3J_{HH}$ = 16.8 Hz, $^3J_{HP}$ = 6.8 Hz, 1H), 4.18 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 3.56 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 1.03 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.95 (t, $^3J_{HH}$ = 7.2 Hz, 3H).

Diphenyl-*cis*-*β*-styrylphosphine (6′c). Methods D [Δ/AIBN], F [)))))/AIBN], and G [*h*ν/300nm] were used. The purification was the same for each method: **6′c** was purified by chromatography (SiO_2; eluent: *n*-hexane/AcOEt, 9:1) to yield 81% (method D), 40% (method F), and 41% (method G) of **6′c** cis as a white solid: ^{31}P NMR (32.44 MHz, C_6D_6) δ −24.8 (m); ^{1}H NMR (80.13 MHz, C_6D_6) δ 7.65−6.90 (m, 11H), 6.40 (dd, $^2J_{HP}$ = 2.4 Hz, $^3J_{HH}$ = 12.6 Hz, 1H); ^{13}C NMR (62.90 MHz, C_6D_6) δ 144.31 (d, $^2J_{CP}$ = 19.1 Hz), 140.03 (d, $^1J_{CP}$ = 10.8 Hz), 137.52 (s), 133.23 (d, $^2J_{CP}$ = 19.2 Hz), 130.14 (d, $^1J_{CP}$ = 8.2 Hz), 128.60 (m); IR (CH_2Cl_2, cm^{-1}) 3051 (Ph), 1438 (C═C); MS (EI) *m*/*z* 288 (M)$^{+\bullet}$.

(1-Hexenyl)diphenylphosphine (7′c). This adduct was synthetized by method G [*h*ν, 300nm, 19 h]. The deuteriated toluene was evaporated. The colorless oil obtained was extracted with *n*-hexane. The solution was concentrated and placed at low temperature. The precipitate was separated and purified by chromatography (SiO_2; eluent: *n*-hexane/AcOEt, 9:1). The product **7′c** was obtained with a yield of 41% (93% cis isomer/7% trans isomer) as a white solid: ^{31}P NMR (32.44 MHz, C_6D_6) δ −14.1 (m) (cis isomer) (93%), −31.7 (m) (trans isomer) (7%); ^{1}H NMR (250.13 MHz, C_6D_6) (ratio cis/trans, 93:7) δ 7.48−7.06 (m, 20H), 6.35−6.18 (m, 4H), 2.70−2.52 (m, 2H), 2.09−1.89 (m, 2H), 1.47−1.11 (m, 8H), 0.92−0.69 (m, 6H); ^{13}C NMR (62.90 MHz, C_6D_6) (ratio cis/trans, 93:7) δ 149.01 (d, $^2J_{CP}$ = 33.6 Hz), 147.96 (d, $^2J_{CP}$ = 24.8 Hz), 140.29 (d, $^1J_{CP}$ = 10.5 Hz), 140.08 (d, $^1J_{CP}$ = 10.6 Hz), 133.07 (d, $^1J_{CP}$ = 19.0 Hz), 133.04 (d, $^1J_{CP}$ = 18.5 Hz), 128.82−127.69 (m), 35.04 (d, $^3J_{CP}$ = 12.8 Hz), 31.71 (s), 31.19 (d, $^3J_{CP}$ = 11.9 Hz), 30.95 (s), 22.61 (s), 22.57 (s), 14.20 (s), 14.16 (s); IR (C_6D_6, cm^{-1}) (ratio cis/trans, 93:7) 3054 (Ph), 1434 (C═C); MS (EI) *m*/*z* 268 (M)$^{+\bullet}$, 239 (M − CH_2CH_3)$^+$, 108 (PhP)$^{+\bullet}$. Anal. Calcd for $C_{18}H_{21}P$: C, 80.57; H, 7.89. Found: C, 80.63; H, 7.99.

(3-Oxo-1-phenylbutyl)diphenylphosphine Oxide (2′d). Methods A [Δ/KOH], B [)))))/KOH], C [Al_2O_3/KOH], and G [*h*ν, 300nm, 39 h] were used to obtain **2′d**.

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Purification after Methods A and B. The solution of acetonitrile was separated from the aqueous phase, evaporated, and taken up in *n*-hexane. The precipitate formed was separated, the supernatent was purified by chromatography (SiO_2; eluent: AcOEt/*n*-hexane, 8:2), and the adduct **2′d** was obtained after recrystallization from EtOH (77% for the method A, 59% for the method B).

Purification after Method C. The solid support was extracted with acetone and the solvent was removed under vacuum. Compound **2′d** was precipitated as a white solid in the mixture $ClCH_2CH_2Cl$/*n*-hexane, separated, and dried to yield 75%.

Purification after Method G. The compound obtained in the mixture after 39 h under irradiation was **2′c** but was oxidized during the purification to give **2′d**. After evaporation of the deuteriated chloroform, the yellow oil obtained was taken up in a mixture $ClCH_2CH_2Cl$/*n*-hexane and the compound **2′d** was precipitated at low temperature (76%): mp 170 °C (from EtOH); ^{31}P NMR (32.44 MHz, $CDCl_3$) δ 33.6 (m); ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.11−7.26 (m, 15H), 4.39 (ddd, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^2J_{HP}$ = 7.2 Hz, 1H), 3.46 (ddd, $^2J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HP}$ = 5.4 Hz, 1H), 3.07 (ddd, $^2J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 3.0 Hz, $^3J_{HP}$ = 11.2 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 205.30 (d, $^3J_{CP}$ = 12.8 Hz), 135.77 (d, $^1J_{CP}$ = 5.5 Hz), 135.72−127.14 (m), 132.07 (s), 43.49 (s), 41.08 (d, $^1J_{CP}$ = 68.7 Hz), 30.59 (s); IR ($CDCl_3$, cm^{-1}) 3061 (Ph), 1817 (C═O), 1263 (P═O); MS (EI) *m*/*z* 348 $(M)^{+\bullet}$, 201 $(Ph_2P{=}O)^+$, 77 $(Ph)^+$, 43 $(CH_3C{=}O)^+$. Anal. Calcd for $C_{22}H_{21}O_2P$: C, 75.85; H, 6.08. Found: C, 75.17; H, 5.99.

(2,2-Diphenylethyl)diphenylphosphine Oxide (4′d). This adduct was purified after the synthesis by method B [))))/KOH]. The organic phase was separated from the aqueous phase and was extracted with acetone (3 × 10 mL). Compound **4′d** was recrystallized at low temperature from *n*-hexane to give 48% of a white solid or was purified by chromatography (SiO_2; eluent: CH_2Cl_2/AcOEt, 7:3): R_f 0.59 (CH_2Cl_2/AcOEt, 7:3); mp 213−214 °C (from *n*-hexane); ^{31}P NMR (32.44 MHz, C_6D_6) δ 25.4 (m); ^{1}H NMR (80.13 MHz, C_6D_6) δ 7.73−7.47 (m, 4H), 7.16−6.88 (m, 16H), 4.90 (td, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 11.9 Hz, 1H), 2.87 (dd, $^3J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 10.9 Hz, 2H); ^{13}C NMR (62.90 MHz, DMSO D_6) δ 144.36 (d, $^3J_{CP}$ = 8.0 Hz), 133.77 (d, $^1J_{CP}$ = 96.8 Hz), 131.02−125.92 (m), 44.42 (s), 34.12 (d, $^1J_{CP}$ = 68.0 Hz); IR (KBr, cm^{-1}) 3054 (Ph), 1178 (P═O); MS (EI) *m*/*z* 382 $(M)^{+\bullet}$, 202 $[(M - CH_2CHPh_2) + 1]^{+\bullet}$. Anal. Calcd for $C_{26}H_{23}OP$: C, 81.66; H, 6.06. Found: C, 80.62; H, 6.02.

Ethyl 3,3-Bis(diphenylphosphinyl)propionate (5″d). This compound was synthetized by methods B [))))/KOH] and C [Al_2O_3/KOH] and in Et_2O after 20 min at room temperature (exothermic reaction).

Purification after Method B. The acetonitrile phase was separated from the aqueous phase and was extracted with *n*-hexane (3 × 10 mL). The solution of *n*-hexane contained the compound **5′c** (see purification of **5′c**). The acetonitrile phase was concentrated and was purified by chromatography (SiO_2; eluent: CH_2Cl_2/acetone, 1:1) to yield 20% of **5″d** as a brown oil.

Purification after Method C. The solid support was extracted with MeOH. This solution was purified by chromatography (see Purification after Method B). The yield of **5″d** was 20%.

Purification after Synthesis in Et_2O. The mixture was directly purified by chromatography (same conditions) after 20 min at room temperature to give 73% of **5″d** as a brown oil: ^{31}P NMR (32.44 MHz, $CDCl_3$) δ 31.7 (m); ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.88−7.74 (m, 8H), 7.32−7.25 (m, 12H), 4.27 (tt, $^3J_{HH}$ = 5.7 Hz, $^2J_{HP}$ = 20.1 Hz, 1H), 3.69 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 2.85 (td, $^3J_{HH}$ = 5.7 Hz, $^3J_{HP}$ = 15.0 Hz, 2H), 0.94 (t, $^3J_{HH}$ = 7.2 Hz, 3H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 171.36 (s), 131.90−128.27 (m), 129.93 (d, $^1J_{CP}$ = 21.6 Hz), 61.44 (s), 30.46 (s), 29.28 (s), 13.81 (s); IR ($CDCl_3$, cm^{-1}) 3060 (Ph), 1728 (C═O), 1438 (C-O), 1190 (P═O); MS (EI) *m*/*z* 503 $(M + 1)^{+\bullet}$.

1,2-Bis(diphenylphosphinyl)-1-phenylethane (9). This adduct was obtained after synthesis by methods A [Δ/KOH], B [))))/KOH], and C [Al_2O_3/KOH].

Purification after Methods A and B. The crude product **9** was precipitated in the reaction mixture at room temperature. The precipitate was separated from the supernatant, washed in H_2O, and recrystallized at low temperature from a CH_2Cl_2/*n*-hexane mixture. Yields were 14% after method A and 40% after method B.

Purification after Method C. The compound **9** was extracted with CH_2Cl_2. This solution was concentrated, added to *n*-hexane, and placed at low temperature to yield 16% of **9** as a white solid: mp 169−172 °C (from CH_2Cl_2/*n*-hexane);[30] ^{31}P NMR (101.26 MHz, $CDCl_3$) δ 35.3 (d, $^3J_{PP}$ = 46.8 Hz), 30.0 (d, $^3J_{PP}$ = 46.8 Hz); ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 8.07−6.81 (m, 25 H), 4.26 (dddd, $^3J_{HP}$ = 4.5 Hz, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 1.4 Hz, $^2J_{HP} \sim {}^3J_{HH}$ = 11.6 Hz, 1H), 3.12 (dddd, $^2J_{HH}$ = 15.3 Hz, $^3J_{HH}$ = 11.6 Hz, $^2J_{HP}$ = 2.8 Hz, $^3J_{HP}$ = 3.9 Hz, 1H), 2.8 (dddd, $^3J_{HH}$ = 1.4 Hz, $^2J_{HH}$ = 15.3 Hz, $^2J_{HP}$ = 9.2 Hz, $^3J_{HP}$ = 13.7 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 131.91 (d, $^1J_{CP}$ = 31.8 Hz), 131.53 (d, $^1J_{CP}$ = 20.4 Hz), 132.16−127.01 (m), 39.38 (d, $^1J_{PC}$ = 66 Hz), 30.14 (d, $^1J_{PC}$ = 69 Hz); IR (KBr, cm^{-1}) 3070 (Ph), 1181 (P═O); MS (EI) *m*/*z* 506 $(M)^{+\bullet}$, 305 $(M - 201)^+$, 201 $(Ph_2P{=}O)^+$, 104 $(M - 2 \times 201)^{+\bullet}$, 77 $(Ph)^+$.

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