Recent advances in the use of phosphorus-centered radicals in organic chemistry

Dominique Leca, Louis Fensterbank,* Emmanuel Lacôte* and Max Malacria*

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This *tutorial review* aims at presenting recent contributions dealing with organic chemistry of organophosphorus radicals. The first part briefly lays out the physical organic background of such intermediates. In a second part the use of organophosphorus radicals possessing a P–H bond that can undergo homolytic cleavage as alternative mediators is detailed. The third part is focused on radical additions of phosphorus-centered radicals to unsaturated compounds, an old reaction that is being rejuvenated. Lastly, radical eliminations of phosphorus-centered radical are introduced in the fourth part. Most of the latter are relatively novel reactions, and have never been reviewed previously.

The organic chemistry of phosphorus is based on the rich array of stable compounds featuring a carbon–phosphorus bond. As a consequence, reactions involving organophosphorus radicals have a long history, that has been told previously.[1] These last few years have witnessed a renewed awareness that P-centered radicals (especially those containing P–O bonds) could be of practical synthetic interest. In this review, we wish to present an overview of the recently published results in the field.

Physical organic aspects

The physical aspects underlying the reactivity of P-centered radicals are essential to synthetic chemists and industrialists, who need to know them in order to benefit from the full potentialities offered by phosphorus-containing compounds.

Université Pierre et Marie Curie, Institut de chimie moléculaire (FR 2769), Laboratoire de chimie organique (UMR CNRS 7611), C. 229, 4 place Jussieu, 75005, Paris, France. E-mail: louis.fensterbank@upmc.fr; lacote@ccr.jussieu.fr; max.malacria@upmc.fr; Fax: 33 (0)1 44 27 73 60; Tel: 33 (0)1 44 27 35 85

Reductions, halogen atom abstractions and additions are the most relevant transformations for synthesis. Several authors have determined key rate constants through various physical methods, among which are time-resolved ESR and laser flash photolysis.

Hydrogen abstraction to form phosphonyl radicals is comparable to that of phenyl-substituted silanes (1.2×10^5 $M^{-1}s^{-1}$).[2] On the other hand, Turro showed that phosphinoyl radicals ($R_2P(O)^{\bullet}$) are roughly ten times more prone to reduction by thiophenol than acylphosphinoyl ones.[3] In any case, these rates are much lower than those of addition to double bonds (see below).

Halogen abstraction is the most popular way to generate carbon radicals on an organic substrate, and thus a key feature of any synthetically relevant radical reaction. Ingold measured some rate constants for diethoxyphosphonyl radicals.[4] They follow the same trends as those of standard tin radicals, but are considerably lower. Turro obtained similar results for acylphosphinoyl and phosphinoyl radicals.[5]

The main characteristic of P-centered radicals is their high reactivity towards unsaturated compounds. Indeed, Ingold's

Dominique Leca

Dominique Leca was born in Bastia (France) in 1976. She graduated from the Ecole Polytechnique in Palaiseau (France) in 2000. She obtained her PhD degree from the Université Pierre et Marie Curie in Paris (France), on radical and hypervalent iodine chemistry in 2004 with Prof. Malacria, Dr Lacôte and Prof. Fensterbank. She is currently a postdoctoral researcher at Syngenta Crop Protection in Basel (Switzerland).

Louis Fensterbank

Louis Fensterbank was born in Poitiers in 1967 and raised in Tours. While graduating from the Ecole Superieure de Chimie Industrielle de Lyon (ESCIL) in 1990, he joined the team of Professor Scott McN. Sieburth at the SUNY Stony Brook, worked on silicon-tethered reactions and obtained his PhD in 1993. He was appointed by the CNRS in 1995 as a Chargé de Recherche in Max Malacria's team, and in 2004 Professor at the Université Pierre & Marie Curie. His research interests concern the development of new radical reactions, organometallic catalysis and asymmetric synthesis.

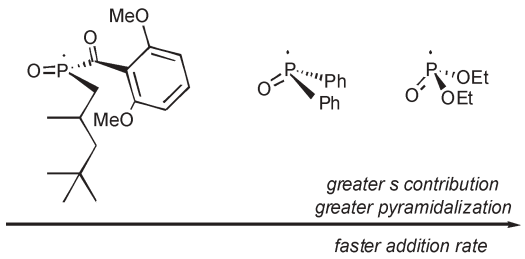


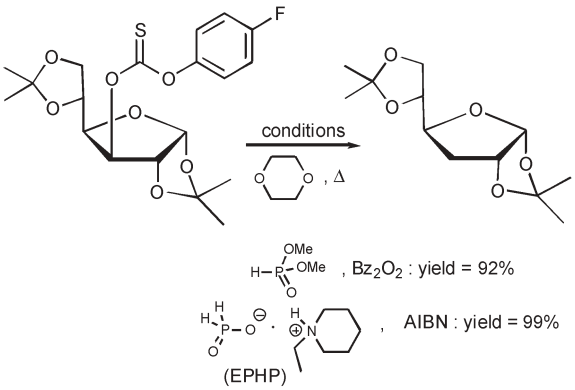
Fig. 1 Geometry of the P-radicals.

diethoxyphosphonyl radicals add easily onto olefins (even hindered ones). Sumiyoshi and Schnabel showed that phosphinoyl radicals also add rapidly onto double bonds,[6] albeit less than phosphonyl ones[7] ($\sim 10^6$–10^7 $M^{-1}s^{-1}$; see Fig. 1). Additional work by Schnabel and Kamachi refined the understanding of the phosphinoyl radicals and confirmed that they added readily onto alkenes.[8] It also confirmed that additions onto electron-poor double bonds occurred faster than addition onto electron-rich ones. Phosphinoyl radicals are thus moderately nucleophilic. Acylphosphinoyl radicals add more slowly. In both cases though, steric effects are much more significant than polar ones.

A considerable amount of work has been spent to link structures and reactivities of the radicals. It had been shown early on that phosphinoyl and phosphonyl radicals were non planar and as a result had a variable degree of s-character.[9,10] Phosphonyl radicals are more bent than phosphinoyl ones. Acylphosphinoyl radicals are further flattened.[5] In general, the more bent the radical, the faster its addition onto olefins (Fig. 1). This trend has been attributed to the relative accessibility of the localized spin to the trapping agent.[3,7]

Use of P-centered radicals as mediators

Radical chemistry has relied on the use of tributyltin hydride (TBTH) as mediator. While extremely useful, this compound is toxic and its by-products are difficult to remove from reaction mixtures. For these reasons, and because radical reactivities are complementary to other reactivities, the quest for alternative mediators has been extremely active.



Scheme 1 Deoxygenation with EPHP.

Barton and Jaszberenyi re-examined some very ancient radical reductions involving hypophosphorous acid. Upon using organic salts of this acid, clean radical reduction, in particular AIBN initiated deoxygenation, was achieved cleanly in refluxing dioxane.[11] The best salt proved to be the *N*-ethylpiperidinium salt (EPHP). Dialkyl phosphonates were also examined, but they require initiation by peroxides and can lead to undesired by-products (Scheme 1).

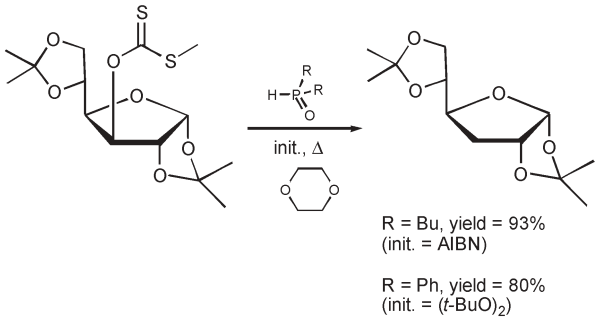
This seminal contribution rapidly spawned several new contributions. In particular, Jang—who contributed to the initial work—showed that the sodium salt of hypophosphorous acid could reduce water soluble organohalides in water.[12] He also introduced dibutylphosphine[13] and diphenylphosphine[14,15] oxides as new reducing agents. Because they are not ionic, they are less hygroscopic than EPHP and thus could be used with water-sensitive substrates. In any case, deoxygenation of hindered substrates was possible. Comparison of

Emmanuel Lacôte

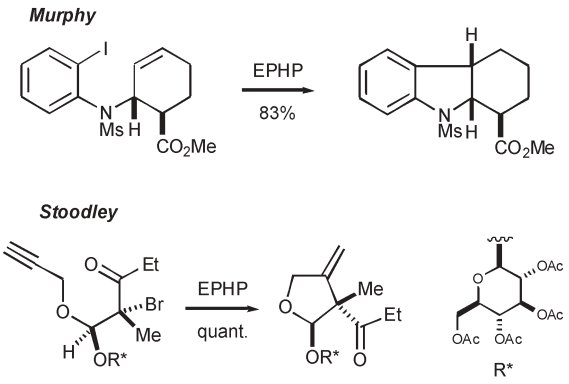
Emmanuel Lacôte was born near Lyon in 1972. After graduating from the École Normale Supérieure, he joined the group of Max Malacria at UPMC. He then moved to Fribourg (Switzerland) for an extended stay in the group of Philippe Renaud, which led to a double PhD from UPMC and the University of Fribourg (1999). After a postdoc at Stanford with Paul Wender devoted to the total synthesis of bryostatin analogues, he was appointed Chargé de Recherche at CNRS in 2000. His current interests involve the use of heteroatoms in organic chemistry and the elaboration of hybrid polyoxometalates toward applications in biology and catalysis.

Max Malacria

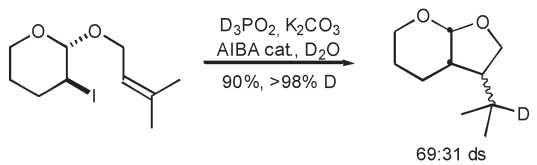
Max Malacria was born in 1949 in Marseille, France. He obtained his PhD from the University of Aix-Marseille III with Professor Marcel Bertrand in 1974. He was appointed Assistant in 1974 at the University of Lyon I with Professor Jacques Goré. After almost two years as a postdoctoral fellow with Professor K. Peter Vollhardt at Berkeley, he went back to the University of Lyon as a Maître de Conférences in 1983. In 1988, he was appointed Full Professor at the UPMC. In 1991, he was appointed junior member of the Institut Universitaire de France, promoted to senior member in 2001. Prof. Malacria has been active in the development of new domino processes in both organometallic and radical chemistry. His current interests lie in the development of new stereoselective reactions involving heteroelements, and platinum-catalyzed reactions.



Scheme 2 Deoxygenation with phosphine oxides.



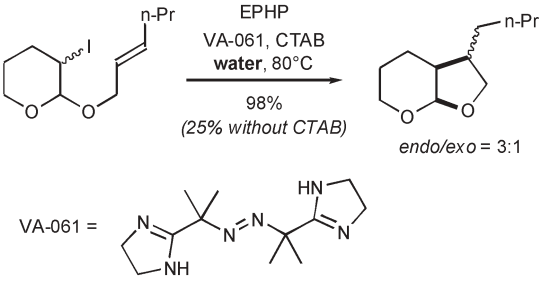
Scheme 3 Cyclizations mediated by EPHP.



Scheme 4 Radical deuteration with phosphorous deuteride.

the yields to those obtained *via* Barton's method shows that the three mediators are complementary.

Once these two main families of P-based mediators had been introduced, rapid progress arose. Murphy and Stoodley simultaneously reported that EPHP could trigger formation of carbon–carbon bonds either through a 6-*exo-trig* cyclization of an aryl radical obtained from an iodide (Murphy),[15] or through a 5-*exo-dig* cyclization of an alkyl α-keto radical



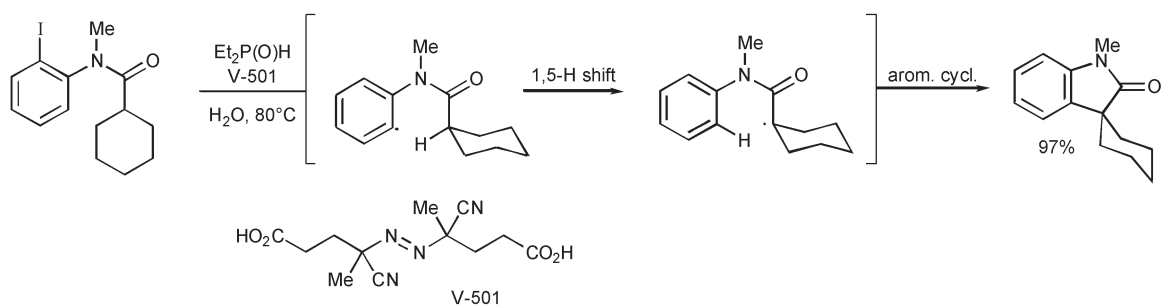
Scheme 5 Radical cyclization in water.

obtained from a bromide (Stoodley).[16] In both cases, yields in densely functionalized products were quite high (Scheme 3).

Oshima introduced deuterated hypophosphorous acid potassium salts to achieve radical deuteration.[17] Deuteration of hydrophobic substrates was possible, albeit the incorporation of deuterium was not optimal because of hydrogen atom abstraction from either the solvent or the various additives used. As water is not prone to transfer a deuterium atom, less hydrophobic subtrates led to deuteration with total incorporation (Scheme 4).

Kita built on the previous studies to report EPHP-mediated cyclization of hydrophobic substrates in water (Scheme 5).[18] This breakthrough was made possible by running the reaction in the presence of a water-soluble initiator (VA-061) and a surfactant (CTAB). The authors explain this outstanding result by a micellar effect generated by CTAB. The organic ammonium probably contributes to the incorporation of the hypophosphoric acid in the micelles. By trapping hypophosphorous acid with a greasy tertiary amine, Jang introduced a surfactant-type chain carrier and reported good yields for deoxygenations of alcohols in water, without additive.[19]

Eventually, Murphy introduced a water-soluble phosphine oxide which permits higher isolated yields than the corresponding reaction using EPHP, with no additional additive (Scheme 6).[20] Upon using diethylphosphine oxide (DEPO), one can carry out sophisticated tin-free tandem radical reactions. Because DEPO is more lipophilic than hypophosphorous acid yet still water-soluble, it can facilitate the interaction between the water-soluble mediator and initiator and the lipophilic substrates without requiring a phase-transfer agent. Moreover, its pK_a is 6, thus ensuring that this almost neutral excess reagent can be extracted into base during workup.



Scheme 6 DEPO-mediated arylation of lactams in water.

One of the most impressive synthetic achievements of the P-based radical mediators is the deoxygenation of an erythromycin B derivative toward the industrial synthesis of ABT-229, a potent motilin receptor agonist. Clean deoxygenation was achieved on a 15 kg scale by using NaH_2PO_2 in an aqueous alcohol, and a phase transfer agent (Scheme 7).[21]

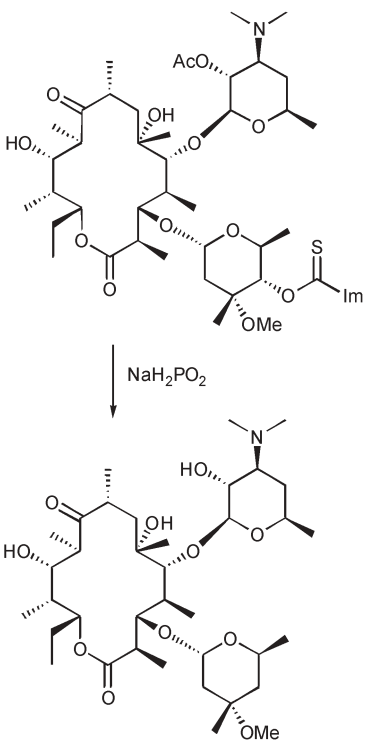
Synthetic applications of P-centered radical additions

Additions of P-based radicals were the first reported reactions of those reactive intermediates.[1a] They suffered around two decades of relative neglect, but are once again being investigated actively.

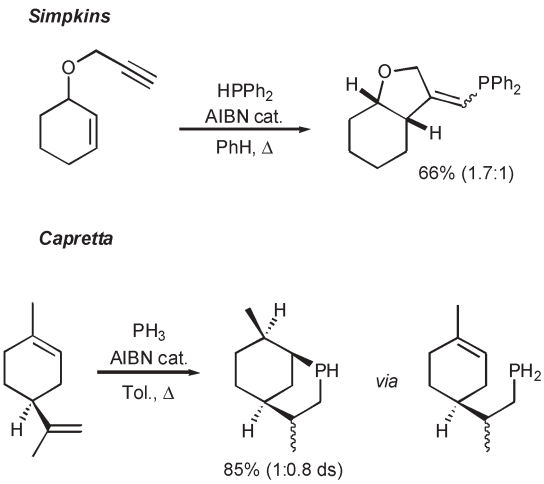
Phosphinyl radicals

Because of the central role of phosphines as ligands for organometallic transformations, radical addition of phosphines to olefins has been pursued, despite its being the oldest radical transformation involving phosphorus. Progress has been sought toward tandem reactions. Simpkins has reported the domino preparation of bicyclic molecules triggered by initial addition of the diphenylphosphinyl radical to various unsaturated compounds (Scheme 8).[22] Capretta used phosphine to add to limonene, a chiral pool terpene. This different approach relied on the bidirectional functionalization of phosphine and yielded a strained bicyclic chiral phosphine in excellent yield.[23]

Oshima introduced very recently a highly elegant mild synthesis of vinylic diphosphines that provides an entry to organic compounds usable in material chemistry. In this process, the two phosphorus atoms were introduced in one single pot through *in situ* formation of tetraphenyldiphosphine, homolytic cleavage of the P–P bond, highly chemoselective addition of the diphenylphosphinyl radical to a terminal alkyne, and homolytic substitution on the diphosphine to regenerate a diphenylphosphinyl radical (Scheme 9).[24]



Scheme 7 Use of phosphorous acid in synthesis.



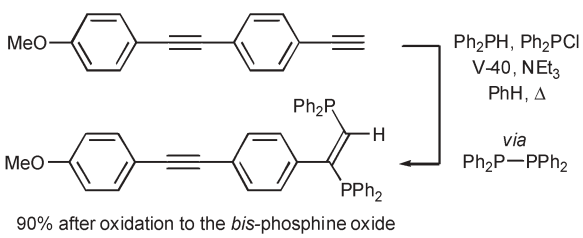
Scheme 8 Additions of phosphinyl radicals.

Phosphonyl radicals

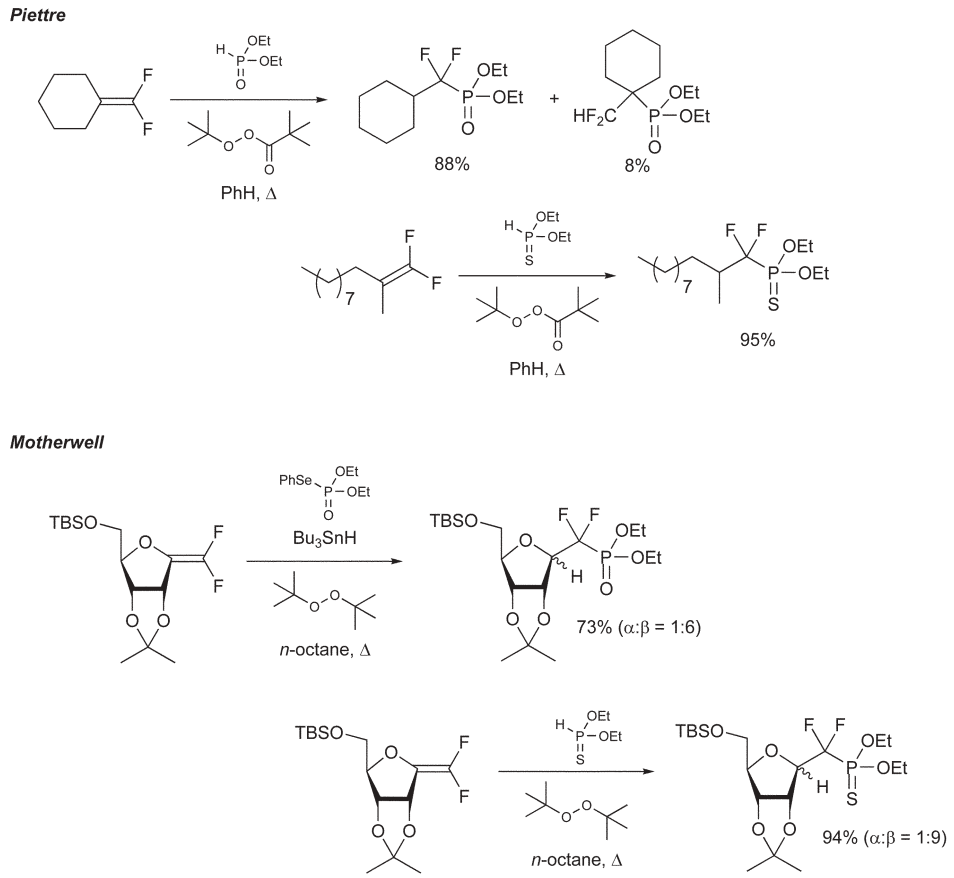
By taking advantage of the rapid β-elimination of iodo radicals, Russell has devised a vinylation of phosphonyl radicals derived from mercury compounds.[25] Probably because of the toxicity of mercuric salts, this method has not been followed by synthetic applications. Piettre[26] and Motherwell[27] simultaneously used the very efficient addition of phosphonyl radicals to alkenes to prepare 1,1-difluorophosphonates, which are believed to be isosteric to phosphates and thus of high interest in pharmacology. Both authors' disconnections relied on the addition of phosphonyl radicals to difluoro-olefins (Scheme 10). By using difluoroenol ethers derived from sugars, Motherwell was able to achieve total regioselectivity.

Phosphonyl radicals have subsequently been involved in tandem and cascade processes. Observing that the phosphonyl radicals used as mediators in the radical cyclization of dienes also led to the formation of phosphonate by-products, Parsons was able to cleanly prepare the corresponding cyclic organophosphorus derivatives in good yields (Scheme 11).[28]

Renaud introduced a new tandem reaction based on the addition of phosphonyl radicals, radical translocation and final cyclization onto the vinylphosphonate. Various cyclopentane derivatives could be prepared (Scheme 11).[29]



Scheme 9 Diphosphinylation of alkynes.



Scheme 10 Additions of phosphonyl radicals to *gem*-difluoro olefins.

Radicals from hypophosphites and phosphinates

Hypophosphite hydrides can add to unsaturated compounds and thus lead to the formation of the corresponding phosphinates. Montchamp was able to carry out this process at room temperature thanks to the triethylborane/air initiating system (Scheme 12).[30]

His study showed that formation of a radical from non-substituted hypophosphite salts or esters was much easier than from the mono-substituted phosphinates; that H-abstraction from the alkylesters appears easier than from the salts; that the hypophosphite radicals were relatively electrophilic.

Piettre has extended the scope of those radicals to the preparation of previously unreported α,α-difluorophosphinates. Radicals derived from the hypophosphorous acid sodium salt proved more reactive than both phosphonyl or phosphonothioyl radicals.[31]

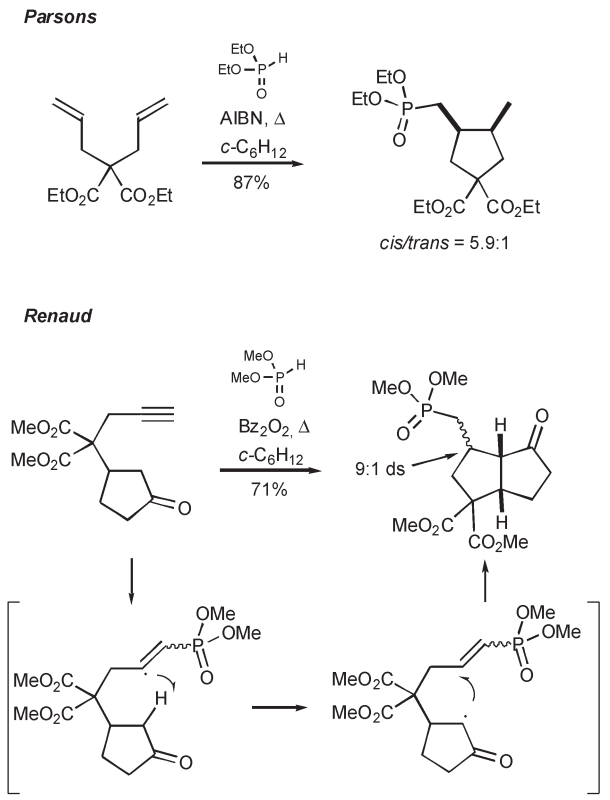
Fukuyama designed a highly elegant synthesis of indoles by reacting hypophosphite salts with unsaturated thioanilides.[32] Initial regioselective addition of the P-centered radical onto the C=S bond generated a new stabilized carbon radical that could cyclize onto the double bond in the *ortho* position, thus giving birth to the carbon-skeleton of indoles. Aromatization of the compound generated the desired 2,3-substituted indoles. The author used this reaction as the key-step toward the total synthesis of (±)-catharantine, a presumed biological precursor of the antitumor alkaloids vinblastine and vincristine (Scheme 13).

Phosphinoyl radicals

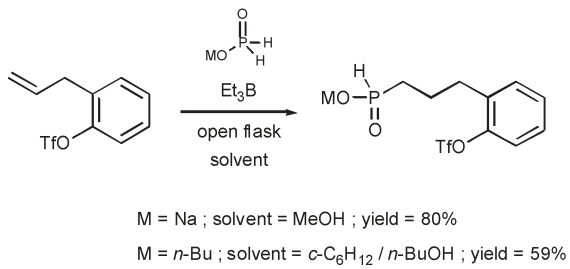
Synthetic uses of additions of phosphinoyl radicals are relatively less abundant than what could have been expected when considering their popularity in polymer chemistry, spectroscopy, and as mediators (see above). Nonetheless, those radicals have been showed to be attractive addition partners. Taillades showed that methanol was the best solvent to carry out radical addition of diphenylphosphine oxide onto olefins at room temperature,[33] while Parsons reported the synthesis of a phosphorus-containing cyclic hydrazine through a radical tandem involving an hydrazone as the last radical acceptor.[28]

Thiophosphonyl and other sulfur-containing radicals

As part of the work described previously, Piettre[26] and Motherwell[27] examined the reactivity of thiophosphonyl radicals (Scheme 10). Both authors observed that thiophosphonyl radicals led to higher yields. Motherwell attributed this improvement to the increased efficiency of the H-transfer step, due to a weaker P–H bond in thiophosphonates. This is consistent with further work by Piettre, who carried out the same addition at room temperature using the ethyl radicals obtained from aerobic decomposition of triethylborane as the initiators.[34] In the same conditions, the corresponding phosphonates are left unchanged.

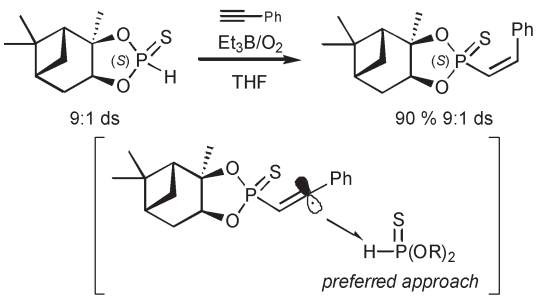


Scheme 11 Use of phosphonyl radicals for tin-free cascade processes.



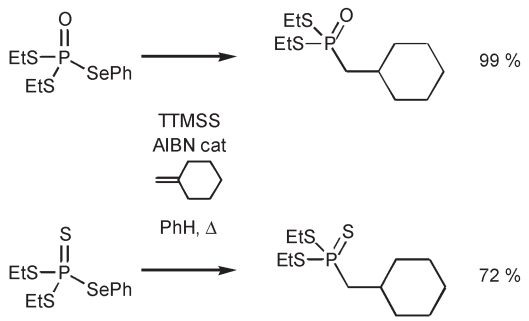
Scheme 12 Triethylborane/air-mediated formation of phosphinates.

Parsons introduced a chiral thiophosphite (Scheme 14).[35] Absolute configuration on phosphorus was retained. The *Z*-olefin was obtained from phenylacetylene, showing that approach of the bulky reductant to the intermediate radical was the determining factor.

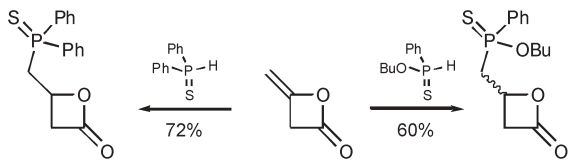


Scheme 14 Addition of chiral thiophosphites.

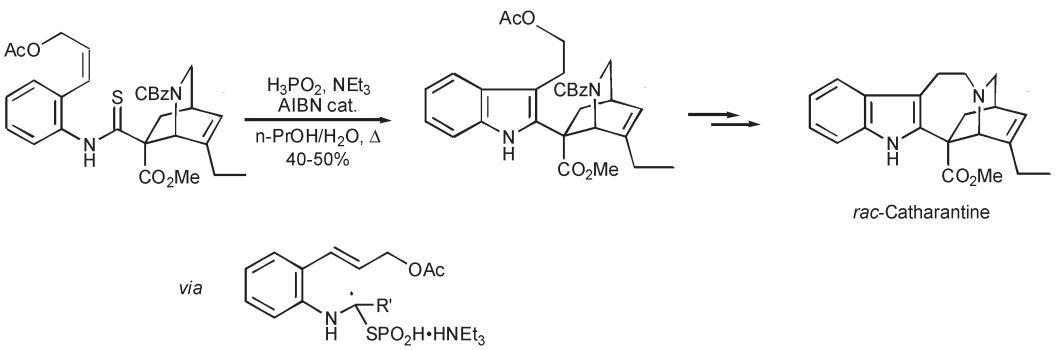
Other sulfur-containing radicals were studied. The main results were published by Piettre, who used the homolytic cleavage of a P–Se bond introduced by Motherwell to access previously unknown *S*,*S*-dialkylphosphonodithioyl and phosphonotrithioyl radicals.[36] Those intermediates added smoothly onto olefins and were tentatively attributed a rather nucleophilic character. If confirmed, this latter result would be of high practical importance, since the philicity of the radical could be fine-tuned by simple choice of the substituents on phosphorus (Scheme 15).



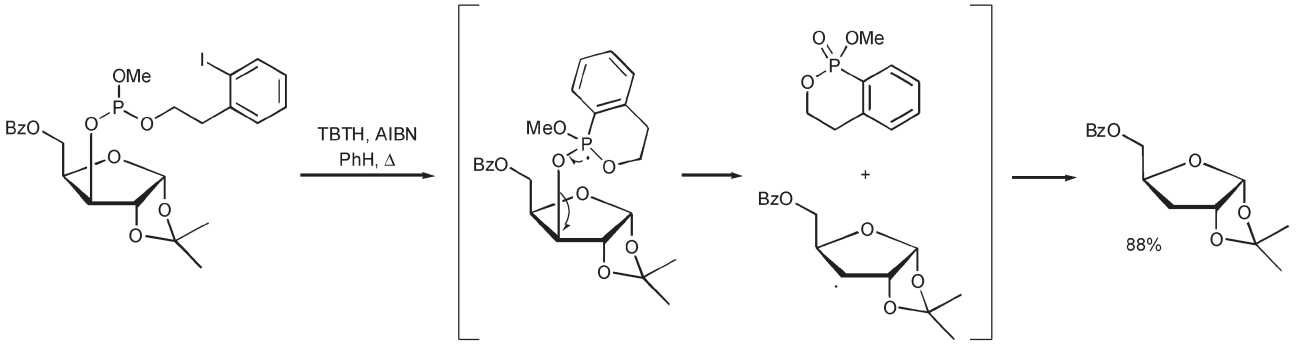
Scheme 15 Addition of phosphono di- and tri-thioates.



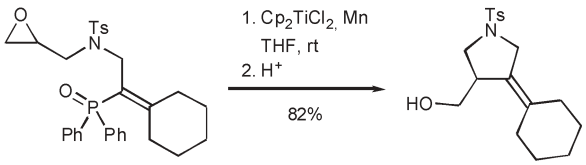
Scheme 16 Addition of thiophosphine oxides and thiophosphinates.



Scheme 13 Formation of indoles from thioanilides.



Scheme 17 Radical deoxygenation through phosphoranyl radicals.



Scheme 18 Elimination of β-phosphinoyl radicals.

Tuck had previously published an entry to phosphorus-containing β-lactones, which were obtained by addition of various P-centered radicals to diketene. In particular, radicals produced from diphenylphosphine sulfide or thiophosphinates reacted smoothly and gave fair yields of the desired lactones (Scheme 16).[37]

Elimination of organophosphorus radicals

Phosphoranyl radicals

Phosphoranyl radical reactivity (and notably elimination) has been extensively reviewed in the past.[1c,d]

Chatgilialoglu built on the affinity of silyl radicals for sulfur and selenium atoms to devise a radical method to reduce phosphine sulfides and selenides to phosphines.[38] Initial results show that the reactions proceed with retention of configuration.

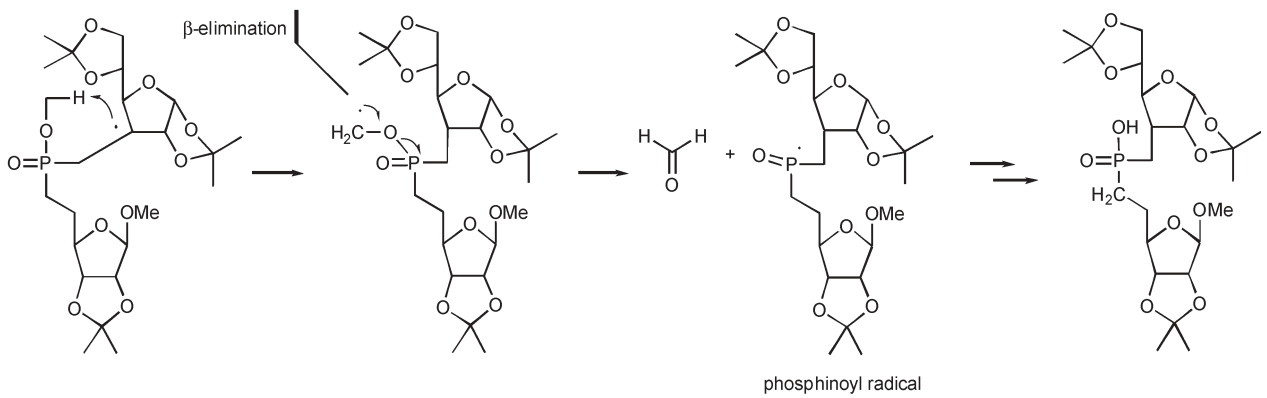
Koreeda used the phosphoranyl radicals β-scission pathway to achieve versatile deoxygenation of alcohols (Scheme 17).[39] The method works best with hindered alcohols, especially tertiary ones. Besides, the phosphonate by-product is easily removed from the desired compound. These two features ensure that this method is an attractive alternative to the Barton–McCombie deoxygenation of alcohols.

β-Elimination of P-centered radicals

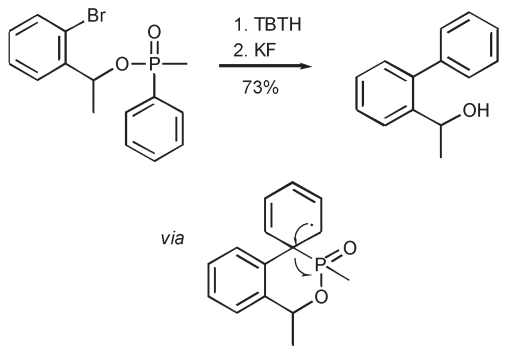
It has been known for quite a long time that addition of phosphinyl radicals to olefins were reversible.[40] However, until recently, no work had addressed the β-elimination of P(V)-based radicals. We were the first to report one such reaction, after we serendipitously observed that β-phosphinoyl radicals could indeed undergo elimination. In our initial report, this pathway accounted for a minor product of the reaction.[41] We could nonetheless optimize the reaction, which proceeds at room temperature and is a formal radical vinylation (Scheme 18).[42]

En route to the synthesis of modified oligonucleotides through addition of hypophosphorous salts to suitable sugars, Piettre reported the unforeseen β-elimination of a phosphinoyl radical from a phosphinate (Scheme 19).[43] This example demonstrates further that β-phosphinoyl radicals are prone to undergo elimination, even when the substituents are all alkyl groups.

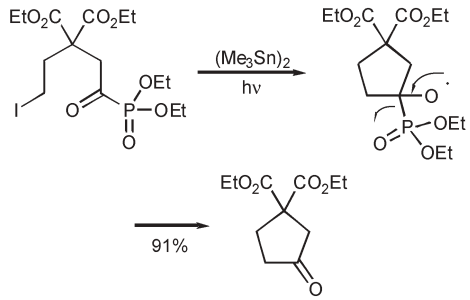
Other oxidized P-centered radicals have since been shown to undergo β-elimination. Clive used such a process to prepare biaryls *via ipso*-substitution on arylphosphinates. Elimination from the intermediate radical is probably driven by rearomatization to the biarylic compound (Scheme 20).[44]



Scheme 19 Elimination of an alkyl β-phosphinoyl radical.



Scheme 20 Biaryl formation through *ipso*-substitution of arylphosphinates.



Scheme 21 Preparation of cyclic ketones *via* β-phosphonyl radical elimination.

Eventually, Kim introduced the β-elimination of a phosphonate radical from an alkoxy radical to prepare cyclic ketones (Scheme 21).[45] His reaction allows intramolecular acylation of radicals, using an acylphosphonate as the key-carbonylating agent. In that perspective, Kim's acylation and our vinylation (Scheme 18) are quite complementary.

Conclusion and perspectives

The growing awareness for green and sustainable methods stemmed by legitimate concerns for the environment gives a strong and renewed relevance to the development of radical reactions involving phosphorus. Work in this field has moved from the understanding of physical aspects underlying the reactivities to optimization of the latter, and their use in total synthesis of complex molecules. Further progress should come from the introduction of more atom-efficient and stereoselective methods. Given the existing knowledge concerning phosphorus-containing compounds, progress will certainly also be achieved by integrating radical steps in more complex one-pot and domino processes.

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