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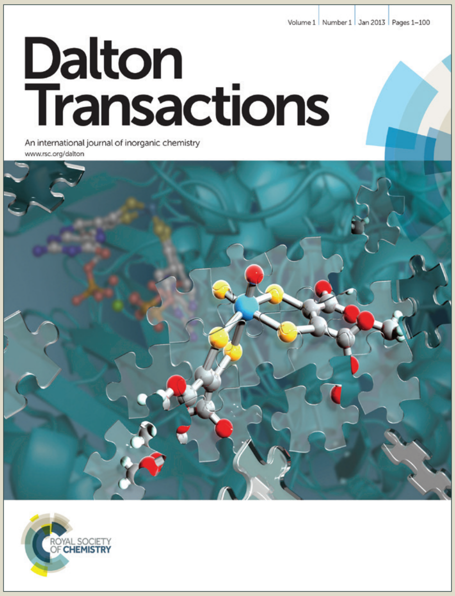

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Dehydrogenative Coupling Involving P(O)-H Bonds: a Powerful Way for the Preparation of Phosphoryl Compounds

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Because of the unique properties and wide applications, continuing efforts have been devoted to developing simpler and cleaner methods for the synthesis of organophosphorus compounds. Recently, transition metal-catalysed dehydrogenative coupling has been emerging as one of the powerful methodologies for constructing chemical bonds. Herein, we highlight the recent progress in the preparation of organophosphorus compounds *via* transition metal-catalysed dehydrogenative couplings of P(O)H compounds with Z-H compounds.

Introduction

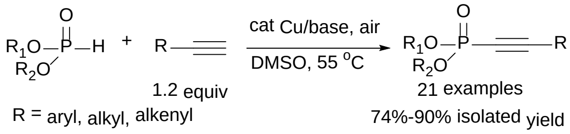
Organophosphorus compounds have wide applications in medicinal chemistry, materials science, agrochemistry and organic synthesis.[1] However, their preparation usually heavily depends on traditional methods which use halophosphorus compounds $R_{3-n}P(O)X_n$ as starting materials, i.e. the Friedel-Crafts type reaction of PCl_3 with benzene generating $PhPCl_2$, and nucleophilic substitutions of $R_{3-n}P(O)X_n$ with organolithiums or Grignard reagents etc.[1,2a] The Michaelis–Arbuzov reaction (the reaction of phosphites with organohalides generating phosphonates) is also a popular way for their preparation.[2b] It is clear that these traditional methods need modernization since they no longer satisfy the criteria of modern synthesis featuring high efficiency, selectivity and functional tolerance. Although such modernization progress was slow in the past, it has increased considerably in recent years, as exemplified by those newly developed efficient C-P bond formations catalyzed by metal catalysts.[2c-2h]

$$E{-}H \;+\; Z{-}H \xrightarrow[-2[H]]{\text{cat M}} E{-}Z \qquad (1)$$

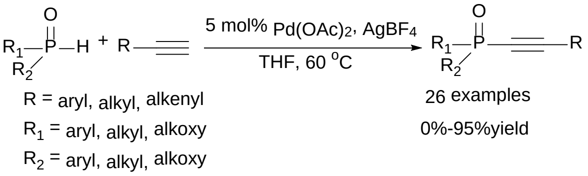
Transition metal-catalysed dehydrogenative coupling is an attractive straightforward way for the construction of chemical bonds (Eq 1).[3] Herein, we summarize recent studies on the synthesis of organophosphorus compounds *via* this strategy.

Constructing *sp*C-P bonds

The first dehydrogenative coupling of terminal alkynes with $(RO)_2P(O)H$ forming alkynylphosphonates was reported in 2009 (Scheme 1).[4] In the presence of 10 mol% CuI and 20 mol% Et_3N, phenylacetylene coupled readily with diisopropyl phosphite in DMSO at 55 °C under air to produce the corresponding phenylethynylphosphonate in 89% yield. Both aromatic and aliphatic terminal alkynes including those with functional groups are applicable to this reaction. The synthetic value was further displayed by the synthesis of phosphonates bearing a norethindrone and nucleotide fragment. However, this reaction only proceeded well with hydrogen phosphonates $(RO)_2P(O)H$. For example, a secondary phosphine oxide like $Ph_2P(O)H$ was oxided to diphenylphosphinic acid and no corresponding coupling product was generated under similar reaction conditions.[5] Despite this limitation, this finding provides the basic platform for constructing *sp*C-P bonds *via* cross dehydrogenative couplings.[4-8]

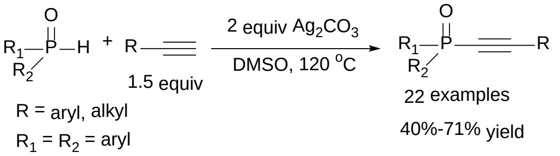


Scheme 1 Copper-catalysed aerobic oxidative dehydrogenative couplings between H-phosphonates and terminal alkynes.



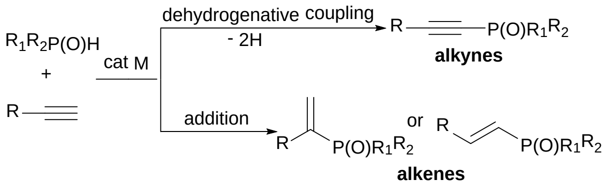
Scheme 2 Palladium-catalysed dehydrogenative couplings between P(O)H compounds and terminal alkynes.

Recently, a palladium-catalysed *sp*C-P bond forming reaction was disclosed (Scheme 2).[7] Mediated by 5 mol% $Pd(OAc)_2$ and 2 equiv $AgBF_4$, all of the three hydrogen phosphoryl compounds, H-phosphonates, H-phosphinates and secondary phosphine oxides, could be coupled with terminal alkynes in THF at 60 °C. This reaction overcomes the substrate's limitation problem of the Cu-catalyzed aerobic oxidative dehydrocouplings, and provides a general access to alkynylphosphoryl compounds under a mild reaction condition, albeit a stoichiometric amount of $AgBF_4$ was required. At the same time, Lei reported similar cross dehydrogenative couplings between secondary phosphine oxides and terminal alkynes (Scheme 3).[8] Various alkynyldiarylphosphine oxides were produced in moderate yields in DMSO at an elevated temperature employing 2 equiv Ag_2CO_3 as an oxidant.



Scheme 3 Silver-mediated dehydrogenative couplings between diarylphosphine oxides and terminal alkynes.

It is worth noting that, from the same combination of a P(O)H compound with an alkyne, an alkenylphosphoryl compound can be produced efficiently *via* selective addition of P(O)-H bond to an alkyne, under different conditions (Scheme 4).[2g] Therefore, both of the two basic classes of organophosphoryl compounds, alkene and alkyne, can be prepared from the same chemical feedstock. Currently, little is known about the mechanistic aspects of the above-mentioned dehydrocouplings. It is expected that future studies on the mechanism can provide new clues to the catalysis leading to the discovery of a more efficient and practical dehydrocoupling reaction for the synthesis of the corresponding phosphorylalkynes.

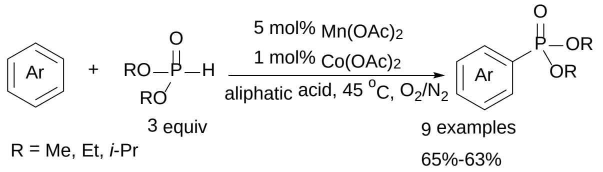


Scheme 4 Metal-catalyzed reactions of P(O)H compounds with alkynes generating either alkynes or alkenes.

Constructing sp^2C-P bonds

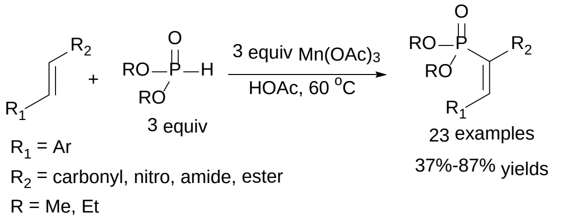
In 1962, Jason disclosed the phosphorylation of naphthalene with diethyl phosphite in the presence of a stoichiometric amount of *t*-butyl peroxide at 130-150 °C.[9] Despite the low yield of the products, this reaction represented a pioneering early example of sp^2C-P bond formation *via* cross dehydrogenative couplings.[10-32]

In 2006, Ishii reported a $Mn(OAc)_2$ and $Co(OAc)_2$ co-catalysed aerobic oxidative dehydrogenative coupling of arenes with diethyl phosphite in acetic acid to produce arylphosphonates (Scheme 5).[11] Later, Zhang disclosed the phosphorylation of thiazoles, furans, and pyrroles with dialkylphosphites in acetic acid using 3 equiv $Mn(OAc)_3$ as an oxidant.[12] Various phosphonates including those with functional groups like alkoxy, carbonyl, formyl, ester and ether groups were produced in high yields and high selectivity. Under similar reaction conditions, simple arenes were also phosphorylated.[13] Thus, both electron-deficient and electron-rich arenes coupled with diethyl phosphite readily, producing the corresponding arylphosphonates in good yields. The phosphorylation of electron-rich arenes with diphenylphosphine oxide also proceeded to produce the corresponding phosphine oxide in moderate yields.[14]



Scheme 5 Mn and Co co-catalysed dehydrogenative couplings between H-phosphites and simple arenes.

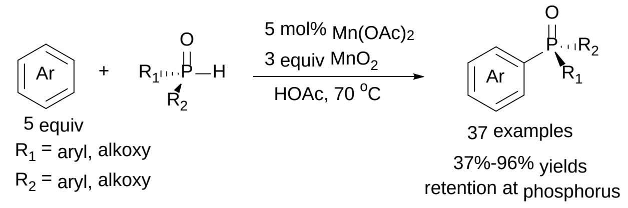
Employing 3 equiv $Mn(OAc)_3$, the phosphorylation of arylalkenes bearing conjugated groups such as ketone, amide, nitro, or ester with dialkylphosphites in acetic acid took place regioselectively at the *α*-position (Scheme 6).[15] This reaction could produce the corresponding (*E*)-alkenylphosphonates in moderate to good yields (37%-87%). Compounds with functional groups such as flavones, coumarins[16a] and uracil[16b] were also prepared by using similar $Mn(OAc)_3$-mediated dehydrogenative couplings.



Scheme 6 Mn-mediated phosphonation of arylalkenes bearing conjugated groups.

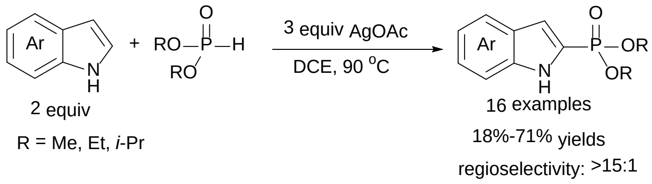
Interestingly, this Mn-mediated radical phosphorylation is applicable to the functionalization of [60]fullerene.[17] Thus, by refluxing a mixture of [60]fullerene, 2 equiv dialkyl phosphites and 2 equiv $Mn(OAc)_3$ in chlorobenzene for 50 min, a singly-bonded fullerene dimer was generated as a meso and racemic isomeric mixture in 28%-34% yields.[17a] By adjusting the ratio of the starting materials, the hydrophosphorylated fullerenes ([60]fullerene/dialkyl phosphites/$Mn(OAc)_3$ = 1:10:2) and acetoxyphosphorylated fullerenes ([60]fullerene/dialkyl phosphites/$Mn(OAc)_3$ = 1:2:10) were also produced selectively.[17b]

In 2014, Montchamp reported a $Mn(OAc)_2$-catalysed sp^2C-P bond forming reactions *via* dehydrogenative coupling between arenes and P(O)H compounds (Scheme 7).[18] In the presence of 5 mol% $Mn(OAc)_2$, 3 equiv MnO_2 and 3 equiv NaOAc, various arenes coupled with H-phosphinates in acetic acid at 70 °C to produce the corresponding phosphoryl compounds in 37%-94% yields. With a chiral P(O)H compound, the dehydrocoupling proceeded with retention of configuration at phosphorus. H-phosphonates and secondary phosphine oxides were also applicable to this reaction.



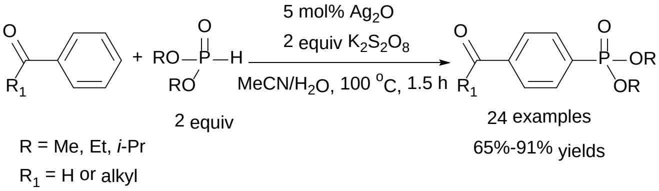
Scheme 7 Mn-catalysed phosphonation of arenes.

A silver-mediated sp^2C-P bond forming reaction *via* dehydrogenative coupling was reported by Wan in 2012 (Scheme 8).[19] Using 3 equiv AgOAc, the bioactive 1*H*-indol-2-ylphosphonates were generated from reactions of indoles with dialkyl phosphonates in DCE at 90 °C in 18%-71% yields. Subsequently, Huang achieved a phosphorylation of furans, thiophenes, thioazoles, pyrroles and pyridines with a catalytic amount $AgNO_3$ using 4 equiv $K_2S_2O_8$ as an oxidant.[20] This dehydrogenative coupling occurred in a biphasic CH_2Cl_2/H_2O system at room temperature affording the heteroarylphosphonates in good yields. Kim also studied dehydrocouplings between substituted pyrroles and dialkyl phosphonates under similar reaction conditions.[21]



Scheme 8 Ag-mediated phosphonation of indoles.

Dehydrogenative couplings mediated by silver were also applicable to the cross coupling of thiazoles with secondary phosphine oxide.[22] For example, by refluxing a mixture of thiazoles, 3 equiv diarylphosphine oxides and 1 equiv $AgNO_3$ in MeCN at 90 °C, the corresponding phosphine oxides could be produced in 19%-92% yields.



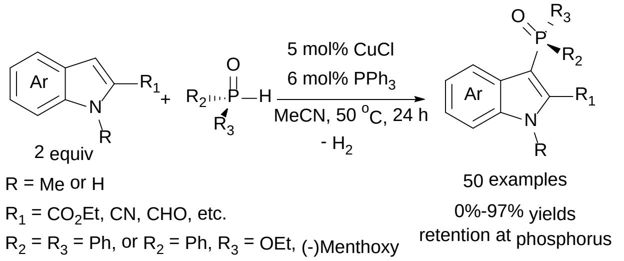
Scheme 9 Ag-mediated phosphonation of aromatic aldehydes and ketones.

In 2015, Huang reported a Ag_2O-mediated dehydrogenative coupling by using 2 equiv $K_2S_2O_8$ as an oxidant (Scheme 9).[23] This reaction features high regioselectivity at the *para*-position. Various formyl and acylphenylphosphonates were synthesized in 65%-91% yields.

Very recently, the C−H bond phosphorylation of ketene dithioacetals with P(O)H compounds was also reported.[24] Interestingly, with secondary phosphine oxides, this transformation could take place with 3 equiv $K_2S_2O_8$ as the oxidant, whereas 3 equiv $AgNO_3$ were required with H-phosphonates.

Copper complexes were also used as catalysts for the construction of sp^2C-P bonds *via* dehydrogenative couplings.[25,26] In 2013, Yang disclosed a copper-catalysed dehydrogenative coupling of *α*-amino carbonyl compounds with diphenylphosphine oxide in the presence of 2 equiv TBHP,[25] to produce the corresponding imidoylphosphonates in 20%-91% yields.

Very recently, Yang also reported a dehydrogenative coupling between indoles and P(O)H compounds with evolution of hydrogen gas (Scheme 10).[26] Various phosphorylated indoles could be produced in good yields. Moreover, *P*-chiral 3-phosphoindoles were also produced stereoselectively. The synthetic value was further displayed by the synthesis of a drug candidate IDX899 under clinical trial.

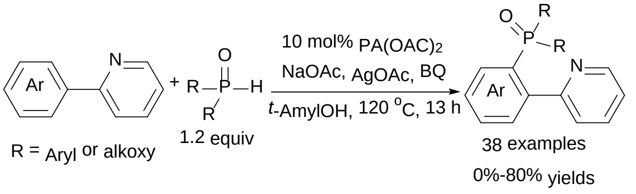


Scheme 10 Cu-catalysed dehydrogenative coupling of indoles with P(O)H compounds.

Palladium was also used to mediate similar dehydrogenative couplings.[27-32] In 2012, Li developed a phosphorylation of azoles with dialkyl phosphites using a palladium catalyst.[27] Thus, using 3 equiv $K_2S_2O_8$, in the presence of 5 mol% $Pd(OAc)_2$ and 30 mol% proline, benzothiazoles coupled with 2 equiv dialkyl phosphites in MeCN at 100 °C to produce the corresponding C_2-phosphonated products in 41%-70% yields. By switching the ligand to bipyridyl, benzoxazoles could also be phosphorylated. Under similar conditions, a selective phosphorylation of coumarins with dialkyl phosphites was reported by Wu.[28] This reaction could be performed under air atmosphere. This transformation also featured high regioselectivity that only the C_3-position in coumarins was phosphorylated.

In 2013, Yu reported a sp^2C-H phosphorylation of benzene rings based on the heterocycle-directed *ortho*-palladation strategy (Scheme 11).[29] Both H-phosphonates and secondary phosphine oxides coupled readily with arenes bearing *N*-heterocyclic substituents to give the corresponding products in

0%-80% yields.[30] This reaction could also be accomplished by an electrochemical process.[31] By using this group-directed strategy, azo compounds could also be phosphorylated.[32]

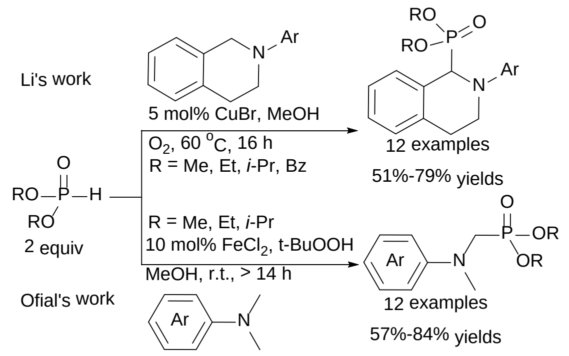


Scheme 11 Pd-catalysed dehydrogenative coupling of arenes with P(O)H compounds.

Many metal-mediated (Pd, Cu, Ag, Mn etc) dehydrocoupling reactions forming sp^2C-P bonds have been developed in recent years. However, as described above, a stoichiometric amount of the metal or oxidant usually has to be used in these reactions. The development of cleaner and simpler, catalytic dehydrocoupling methods is therefore needed for future progress.

Constructing sp^3C-P bonds

sp^3C-P bonds could also be constructed *via* cross dehydrogenative coupling reactions. In 2009, Li disclosed a P(O)-H/sp^3C-H aerobic oxidative dehydrogenative coupling using a copper catalyst to produce *α*-aminophosphonates (Scheme 12).[33] Thus, in the presence of 5 mol% CuBr, H-phosphonates coupled smoothly with *N*-aryltetrahydroisoquinoline in MeOH at 60 °C, affording the corresponding coupling products in good yields. Later, Ofial reported an iron-catalysed oxidative dehydrogenative coupling between *N*,*N*-dialkylanilines and H-phosphonates using *t*-BuOOH as an oxidant (Scheme 12).[34a] Moreover, by increasing the amount of H-phosphonates, the bis-phosphorylation products could also be obtained.[34b]



Scheme 12 Dehydrogenative couplings of tertiary amines with phosphonates catalysed by copper or iron.

Dehydrogenative couplings between P(O)H compounds and tertiary amines (*N*-aryltetrahydroisoquinolines and *N*,*N*-dimethylanilines) were also reported by Zhu in 2012.[35] Mediated by a gold catalyst, the aerobic oxidative dehydrogenative coupling of tertiary amines with both H-phosphonates and secondary phosphine oxides occurred smoothly in MeCN at 60 °C to produce the coupling products *α*-aminophosphonates in 37% to 94% yields.

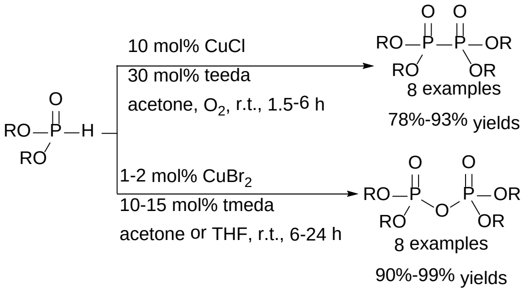
P(O)-H/sp^3C-H dehydrogenative coupling was also realized using visible light catalysts.[36-39] In 2011, Rueping developed a visible light-mediated sp^3C-P bond forming reaction using the photoredox ruthenium/bipyridyl or iridium/bipyridyl catalyst.[36] In a biphasic solution of toluene and water, a variety of *N*-aryltetrahydroisoquinolines were readily phosphorylated with H-phosphonates (3 equiv) to produce the corresponding *α*-aminophosphonates in moderate to high yields. However, dimethylphosphite was not applicable to this reaction due to rapid hydrolysis. This dehydrogenative coupling could also be mediated by a palladium/porphyrin photocatalyst in MeCN.[37] Dimethyl phosphite could also be used as the substrate in this reaction.

Similar coupling reactions also took place using an iridium catalyst immobilized on a polymer.[38] Both H-phosphonates and secondary phosphine oxide were applicable to the reaction which provided smooth coupling with *N*-aryltetrahydroisoquinolines in methanol.

By using eosin Y as a photocatalyst, *N*-aryltetrahydroisoquinolines could also couple efficiently with H-phosphonates.[39] Since this reaction did not use transition metal catalysts, it provided a clean protocol for the synthesis of *α*-aminophosphonates *via* visible light-mediated aerobic oxidative dehydrogenative couplings.

In addition to the reactions described above, this sp^3C-H/P(O)-H dehydrogenative coupling could also be achieved by using MoO_3,[40] iodine,[41] SO_2Cl_2,[42] triarylaminium salts,[43] DDQ[44] and AIBN.[45] However, it should be pointed out that, currently, the sp^3C-H compound was restricted to tertiary amines and an excess amount of P(O)H compounds often were used in these sp^3C-H/P(O)-H dehydrogenative couplings.[46]

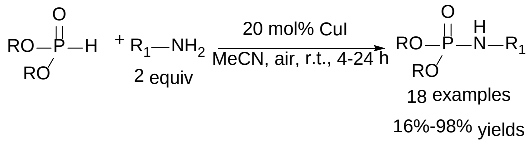
Constructing P-Z (Z = a heteroatom) bonds



Scheme 13 Cu-catalysed dehydrogenative homocoupling of phosphonates.

Aerobic oxidative dehydrogenative homocouplings of H-phosphonates proceeded efficiently in the presence of a copper catalyst (Scheme 13).[47] Surprisingly, the amine ligand can switch the product from P-P products to P-O-P products. Thus, when Et_3N or teeda ($Et_2NCH_2CH_2NEt_2$) was used as the ligand, the copper-catalysed aerobic oxidative dehydrogenative coupling of H-phosphonates produces the P-P coupling products in high yields. In contrast, when tmeda ($Me_2NCH_2CH_2NMe_2$) was employed as the ligand, P-O-P compounds were produced predominately.

Similar cross dehydrogenative couplings between P(O)H compounds and amines also took place readily. Thus, Hayes reported a copper-catalysed aerobic oxidative dehydrogenative coupling between H-phosphonates and amines (Scheme 14).[48] Mediated by 20 mol% CuI, the reaction took place in MeCN at room temperature, affording the corresponding phosphoramidates in moderate to high yield, using an excess amount of amines. This reaction proceeded well with both aromatic and aliphatic primary amines; however, secondary amines gave low yields of the products. Chen and Yu also described similar copper-catalysed dehydrocouplings of H-phosphonates with aromatic amines.[49] We found that, under air at room temperature, by slowly adding P(O)H compounds to amines in ethyl acetate in the presence of CuBr, both H-phosphonates and H-phosphinates coupled readily with aliphatic amines to produce the P-N products in high yields.[50] Moreover, the stereochemistry of this coupling reaction was also investigated showing that an optically pure H-phosphinate coupled with amines with inversion of configuration at phosphorus. We are aware that Mizuno has also disclosed an aerobic oxidative dehydrogenative coupling of H-phosphonates with amides catalysed by a copper catalyst.[51]



Scheme 14 Cu-catalysed aerobic dehydrogenative coupling of phosphonates with amines.

Dehydrogenative couplings generating P(O)-S and P(O)-O bonds were also known.[52] In 1988, Okamoto reported the aerobic oxidative dehydrogenative coupling of H-phosphonates with alcohols in the presence of a copper catalyst.[52a] Similar aerobic oxidative dehydrogenative couplings between H-phosphonates and ArSH were also reported by Kaboudin.[52b]

It should be noted that most of these reactions use H-phosphonates $(RO)_2P(O)H$ as a substrate, i.e. a similar dehydrocoupling reaction with a secondary phosphine oxide $R_2P(O)H$ has not been achieved yet, and there is only one example with H-phosphinate (RO)PhP(O)H.[50,53]

Conclusions

In summary, dehydrogenative coupling reactions are a straightforward and potentially green way for the preparation of organophosphorus compounds. This field has grown quickly in recent years and many new reactions have been developed. However, this field is still immature and there is a lack of general and practically useful dehydrocoupling reactions for the preparation of phosphorus compounds. We expect that with continuing devotion to this field, really efficient and green dehydrogenative couplings, that can replace the conventional methods for the preparation of phosphorus compounds, can be established in the near future.

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Notes and references

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