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Catalytic synthesis and transformations of organophosphorus compounds

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Methods for the catalytic synthesis of organophosphorus compounds with three- and four-coordinate phosphorus and their transformations are summarised. Special attention is given to the synthesis of aryl(vinyl)-substituted phosphonates and phosphinates, as well as aminophosphonates, which are of particular interest due to their high biological activity.

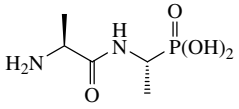
Catalytic synthetic methods that allow the limits of fine organic synthesis to be expanded considerably play a special role in synthetic organic chemistry. Catalytic methods are currently used in synthetic organophosphorus chemistry to obtain various organophosphorus compounds, in particular, functionalised phosphonates and phosphinates, which attract a special attention due to their biological activity.

The diversity of organophosphorus compounds is determined by the position of phosphorus in a periodic system of the elements and by its ability to form one- to six-coordinate phosphorus compounds and bonds with both electropositive and electronegative elements.

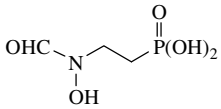
Organic phosphorus derivatives are successfully used as biologically active compounds, complexing reagents, ligands in complexes with transition metals, phosphorus-containing polymers and reagents in organic syntheses.

The biological activity of organophosphorus compounds was not always used for the good of the people. The most toxic organophosphorus compounds, such as fluoro- (or cyano)-containing phosphonates and thiophosphonates behaving as neuroparalytic agents, were created as second-generation chemical weapons (sarin, saman, tabun and VX). These weapons have killed many human lives; furthermore, destruction of such weapons (which is mandatory for all nations that have signed the Convention) presents a major problem (especially for our country) as it requires significant financial expenses.[1]

However, it is owing to the chemical activity of organophosphorus compounds that medical agents such as Alafosfaline and Fosmidomicine were obtained from them.[2]



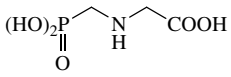
Alafosfaline



Fosmidomicine

The majority of these compounds are the derivatives of α-aminophosphonic acids, *i.e.*, the phosphorus analogues of α-aminocarboxylic acids.

The use of organophosphorus compounds in agriculture as pesticides, plant growth regulators, *etc.*, is of considerable importance.[2] Roundup®, a popular agent, contains fragments of both α-aminocarboxylic and α-aminophosphonic acids.



Glyphosate (Roundup®)

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Maria M. Kabachnik is a candidate of chemical sciences and assistant professor at the Department of Chemistry of M. V. Lomonosov Moscow State University. M. M. Kabachnik is an author of about 250 publications, including 15 inventor certificates and patents. Her scientific interests lie in the chemistry of organophosphorus compounds: development of new methods for the synthesis of compounds of three- and four-coordinate phosphorus and preparation of new biologically active compounds based on natural phosphorus-containing porphyrins.

The complexing capability of diphosphonates gave an opportunity to create a series of organophosphorus complexons, such as hydroxyethylidenediphosphonic acid, ethylenediaminetetramethylphosphonic acid and many others, which have been studied in detail by M. I. Kabachnik *et al*. and used in the extractive metallurgy of non-ferrous metals, trace metals and precious metals.[3–5]

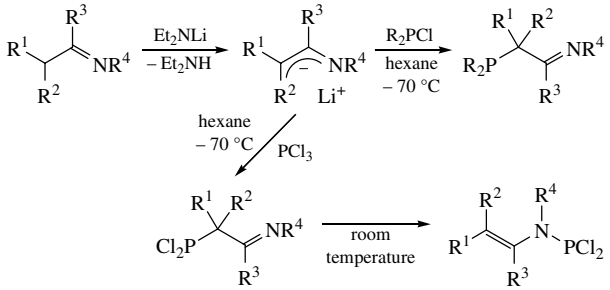
Organic phosphines, phosphites, phosphinites and amidophosphinites are widely used in homogeneous catalysis as ligands in transition-metal complexes.[6–8] The very existence of this area, which is of primary importance in today's chemistry, especially in its infancy, was due to the use of phosphine complexes of palladium, platinum, rhodium, *etc*. The use of transition-metal complexes with chiral phosphine ligands as catalysts is of particular interest when performing asymmetric hydrogenation, hydroformylation and many other reactions. These catalysts enabled the syntheses of enantiomerically pure compounds, including the most significant pharmaceuticals. Many of chiral phosphine ligands became commercially available, though they are difficult to synthesise.

Phosphorus-containing polymers are used less commonly. However, they possess valuable properties, such as fire-resistance and inertness to chemical reagents, which make them interesting from a practical point of view.[9]

Organophosphorus compounds find extensive use in organic synthesis. This primarily includes well-known olefination reactions: Wittig reaction and P–O olefination, that is, the reaction of phosphorus-containing carbanions with carbonyl compounds (the Horner–Woodward–Emmons reaction).

In the majority of reactions, the phosphorus atom acts as a nucleophile. These include the classical Arbuzov, Michaelis–Becker, Pudovik, Kabachnik–Fields and Abramov reactions that allow one to obtain various organophosphorus compounds, as well as the Mitsunobu and Staudinger reactions that provide ways to synthesise diverse organic compounds, such as amines, esters, imides and phosphazo compounds.

There are also reactions where P^{III} or P^{V} compounds act as electrophiles. Among them are the interactions of P^{III} halides with trialkylphosphites[10] or ambident imine anions. In the latter case, dialkylchlorophosphines attack a carbon atom of the ambident system to give functionally substituted phosphines.[11] The use of PCl_3 makes it possible to obtain *N*-phosphorus(III)-substituted enamines; it has been shown that, initially, PCl_3 reacts with these anions at a carbon atom, but then, if the temperature is increased, the PCl_2 group migrates to the nitrogen atom to give phosphorylated enamines (Scheme 1).[12]

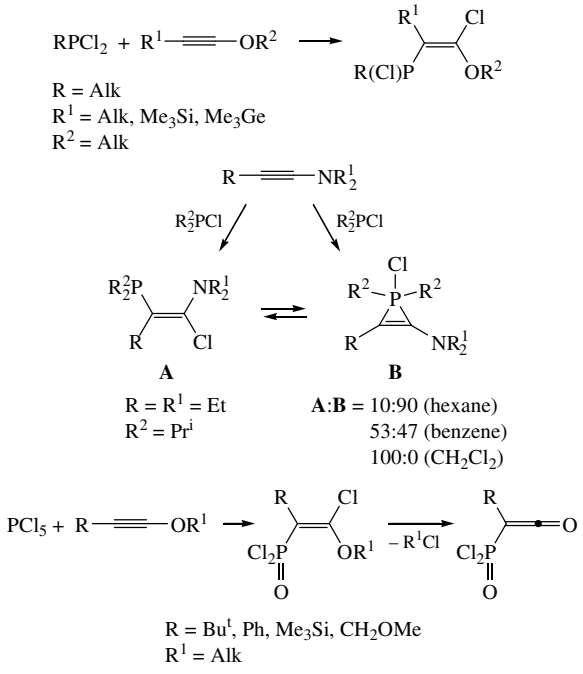


R^1, R^2, R^3 = Alk, H
R, R^4 = Alk

Scheme 1

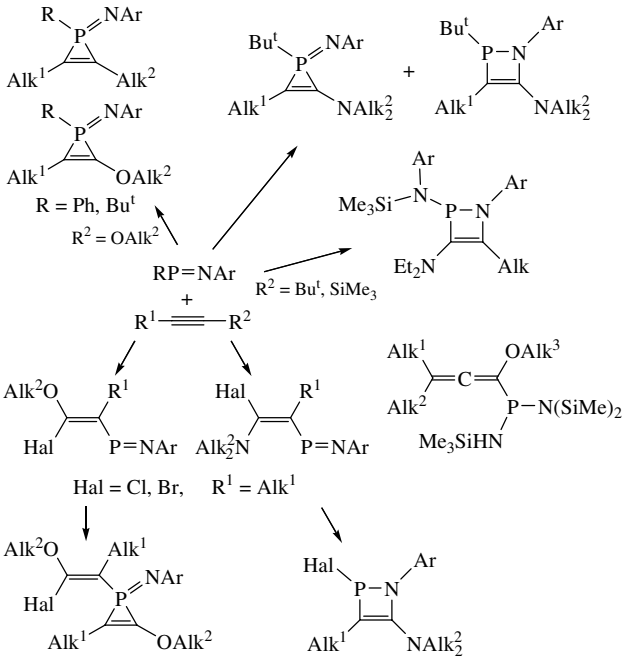
Reactions of R_2PCl, $RPCl_2$ and PCl_5 with electron-donating alkynes containing C_{sp}–OR or C_{sp}–NR_2 bonds involve electrophilic *trans*-addition to the triple bond to give the corresponding phosphorus-containing alkenes (Scheme 2).[13]

The chemistry of low-coordinate phosphorus derivatives is another interesting area in the chemistry of organophosphorus



Scheme 2

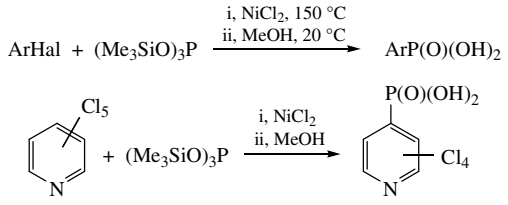
compounds.[14–19] For example, two-coordinate phosphorus derivatives with a P=N bond react with alkynes to give various hitherto-unknown compounds, such as phosphirenes, azaphosphetines and azaphosphabutadienes, depending on the substituents (Scheme 3).[20,21]



Scheme 3

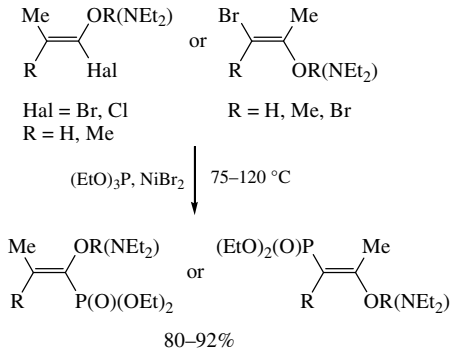
Catalytic substitution producing a C_{sp^2}–P bond

Catalytic reactions with the formation of a C_{sp^2}–P bond proved to be quite efficient in syntheses of aryl and vinyl derivatives of tetracoordinate phosphorus, which were difficult to access before. It is well known that the Arbuzov reaction involving aryl and vinyl halides occurs at high temperatures in the presence of nickel complexes as catalysts.[22–24] The use of trimethylsilylphosphites instead of usual trialkylphosphites allowed us to decrease the reaction temperature and to obtain aryl(hetaryl)-phosphonic acids in high yields after treatment of corresponding arylphosphonates with methanol (Scheme 4).[25,26]



Scheme 4

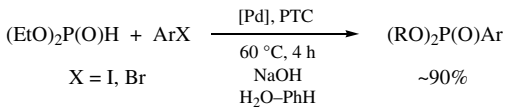
The reaction of trialkylphosphites with substituted vinyl halides allowed us to synthesise a wide range of vinylphosphonates.[27–29] The use of alkenyl halides containing α-alkoxy and α-diethylamino groups made it possible not only to perform this reaction under milder conditions but also to utilize substituted alkenyl chlorides (Scheme 5).



Scheme 5

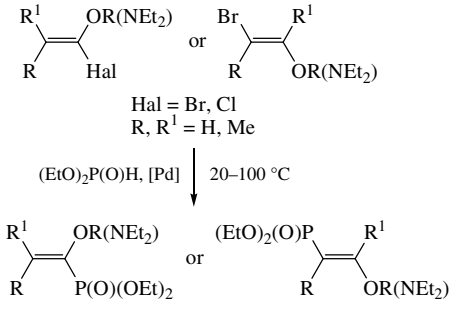
This is not a simple example of cross-coupling, since the catalyst gives rise to a phosphonium salt (or phosphorane), in which Arbuzov rearrangement is likely to occur.

Arylation of dialkylphosphites in the presence of a base catalysed with palladium complexes is the most efficient method to synthesise arylphosphonates.[30–32] These reactions can occur with aryl iodides under mild conditions in aqueous-organic media and involve even 'ligand-free' palladium (palladium acetate was successfully used as a catalyst precursor). Palladium-catalysed arylation of dialkylphosphites can proceed under phase-transfer conditions (50% NaOH, tetrabutylammonium chloride, benzene) in aqueous media (Scheme 6).[33]



Scheme 6

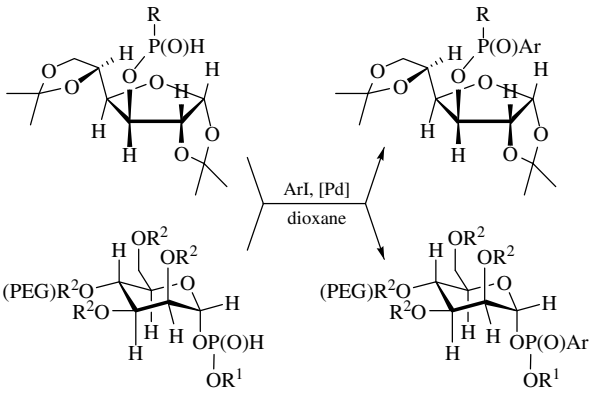
The reaction of substituted vinyl halides with diethylphosphite also occurs under mild conditions to give corresponding vinylphosphonates.[34,35] Unlike the reactions of trialkylphosphites, those of dialkylphosphites with aryl halides or alkenyl halides provide a classical example of cross-coupling to give an sp^2-carbon–phosphorus bond. As in the case of trialkylphosphites, the use of alkenyl halides with α-alkoxy or α-diethyl-



Scheme 7

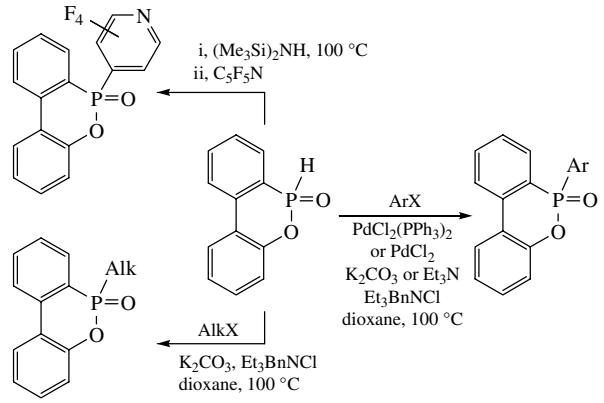
amino groups made it possible to carry out this reaction not only with alkenyl bromides but also with alkenyl chlorides (Scheme 7).[36]

The Pd-catalysed arylation of P^{III}-containing sugars gave arylphosphonates and arylphosphinates of monosaccharide derivatives with pyranose and furanose structures (Scheme 8).[37,38]



Scheme 8

Aside from trialkylphosphites, dialkylphosphites and dialkyl(aryl)phosphine oxides, arylation can be carried out with cyclic arylphosphonites. Scheme 9 shows an example of such arylation catalysed with palladium or nickel, as well as alkylation and S_NAr-substitution with perfluoropyridine.[39]

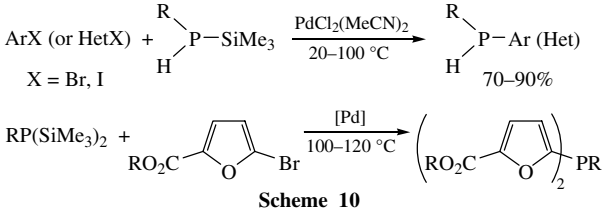


Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, X = I
Ar = Ph, *p*-NCC_6H_4, X = Br

$NiCl_2(PPh_3)_2$	PhI	6 h	100%	
	PhBr	6 h	85%	(^{31}P NMR)

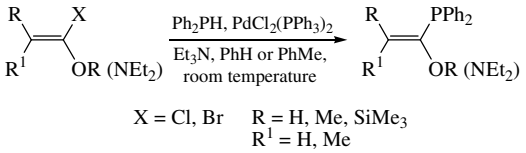
Scheme 9

Stille was the first to obtain tertiary arylphosphines by cross-coupling of Ph_2PSiMe_3 and Ph_2PSnMe_3 with aryl halides catalysed with $PdCl_2(PPh_3)_2$ or $PdCl_2(MeCN)_2$. The reaction was directly analogous to the reaction of Me_3SiNR_2 with ArBr, which was performed previously to yield amines.[40] We used this approach to obtain asymmetrical secondary phosphines. The replacement of hydrogen with a trimethylsilyl group facilitates the reaction and allows one to obtain tertiary phosphines with various substituents at the three-coordinate phosphorus atom. The reaction is employed for the synthesis of water-soluble phosphines (Scheme 10).[41]



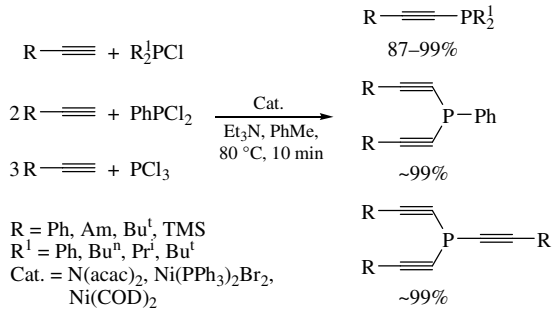
Scheme 10

This reaction can be successfully carried out with diverse vinyl halides to give vinylphosphines with various substituents at the α- or β-position with respect to the phosphorus atom. Of particular interest are α-phosphineneamines obtained by this method; they can be used as ligands in metal-complex catalysis (Scheme 11).[42]



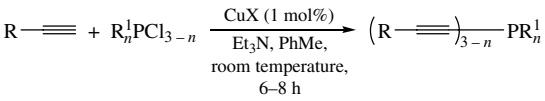
Scheme 11

Alkynyl derivatives of phosphines were obtained by the cross-coupling of R_nPCl_{3-n} with alkynes in the presence of bases, which is more efficiently catalysed with nickel complexes than with palladium complexes.[43]



Scheme 12

This reaction gives mono-, di- or trisubstituted alkynyl derivatives in high yields (Scheme 12). Since these processes occur due to the insertion of Ni^0 into the P–Cl bond, they may be considered as a hetero analogue of Sonogashira reaction. Note that this reaction readily occurs with chlorophosphines, whereas chlorophosphites and amidochlorophosphites do not undergo this transformation. It was found that the problem can be solved using a Cu^I salt as the catalyst (Scheme 13). In this case, the chlorides of three-coordinate phosphorus react under mild conditions to give reaction products in high yields.[44] The reaction may be considered as a catalytic hetero analogue of Custro reaction.



R = Pr, Am, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 3-$F_3CC_6H_4$, $MeOCH_2$, Me_2NCH_2, 2-Py, 2-thienyl, 6-quinolyl
R^1 = Ph, Pr^i, Bu^t, Pr^iO, Et_2N

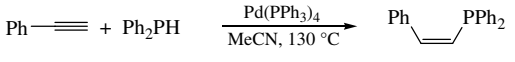
Scheme 13

Addition of compounds with a P–H bond (phosphines and dialkylphosphites) to unsaturated bonds

The addition of secondary phosphines and hydrophosphoryl compounds to activated unsaturated bonds (C=C–Z, C=N and C=O) is a well-known method for the preparation of various organophosphorus compounds, both of three- and four-coordinate phosphorus. The reactivity of organophosphorus compounds in these reactions changes in the order: $Ph_2PH > Ph_2P(S)H > > Ph_2P(O)H > (RO)_2P(O)H$.[45] The addition of compounds with a P–H bond to carbonyl or imine groups is commonly catalysed by Lewis acids. In this case, α-hydroxy- and α-aminoalkylphosphonates with high enantiomeric purity were obtained using chiral ligands.[46,47]

The vinyl derivatives of phosphines can be produced not only by cross-coupling but also by the addition of secondary phosphines to alkynes. The latter reaction, like other addition reactions, is advantageous over substitution, since it better meets the green chemistry requirements (100% atomic efficiency).

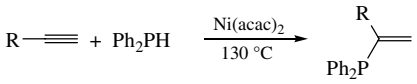
We were the first to perform the hydrophosphination of alkynes catalysed with palladium or nickel complexes and to show that the regioselectivity of the reaction depends on the catalytic system in use and on the alkyne nature. In fact, the reaction of phenylacetylene with diphenylphosphine in the presence of a Pd^0 complex affords only the β-adduct (Scheme 14).[48]



95% (*E*:*Z* = 10:90)

Scheme 14

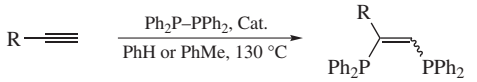
However, we succeeded in finding catalysts and reaction conditions to obtain the α-isomer as the main (and, in some cases, the only) reaction product (Markovnikov product) (Scheme 15).[48]



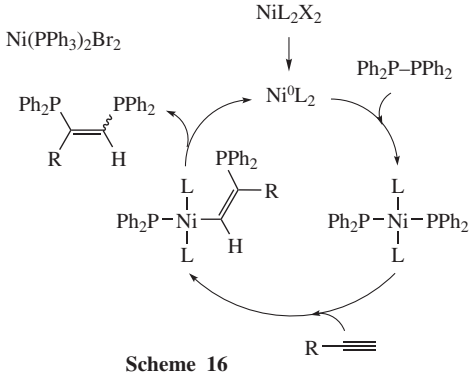
R = Ph, Pr, Am — up to 90%

Scheme 15

We were also the first to perform the addition of a P^{III} compound containing a P–P bond to alkynes under conditions of catalysis with nickel complexes. The test reaction confirms that an alkyne can be inserted into the Ni–P bond (Scheme 16).[49,50]

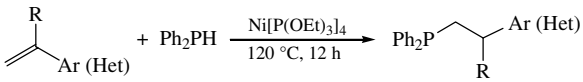


R = Ar, Alk, Het
Ar = Ph, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 3-$F_3CC_6H_4$, 4-NCC_6H_4, naphthyl
Het = 2-Py, 2-thienyl, 6-quinolyl
Alk = Am
Cat. = $NiBr_2$, $Ni(PPh_3)_2Br_2$

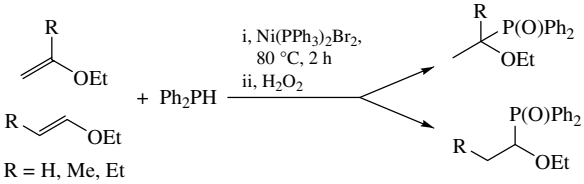


Scheme 16

Secondary phosphines undergo Michael addition to styrenes or alkenes containing electron-withdrawing groups to yield only the β-addition products. On the other hand, the interaction of



R = H, Me — 80–90%
Ar (Het) = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-Py, 4-Py

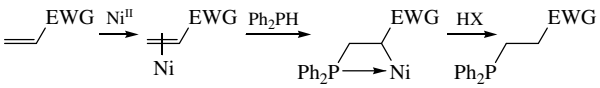


R = H, Me, Et

Scheme 17

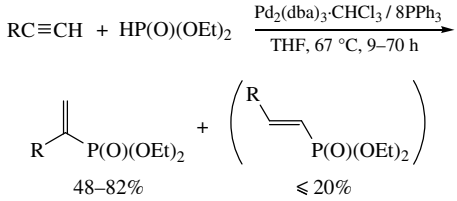
secondary phosphines with alkenes containing electron-donating substituents catalysed with nickel complexes gives exclusively the α-addition products (Scheme 17).[50]

The formation of both anti-Markovnikov and Markovnikov hydrophosphination products may be explained by the electronic effects of substituents within the framework of the Wacker process (Scheme 18).



Scheme 18

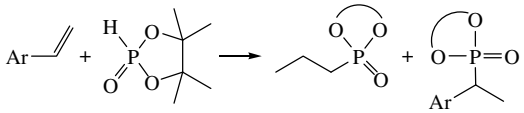
The addition of dialkylphosphite is catalysed with palladium complexes; in the case of aryl-substituted alkynes, it gives a high yield of the α-isomer, *i.e.*, the product of addition according to Markovnikov (Scheme 19).[51]



R = Ph, 4-MeOC$_6$H$_4$, 6-MeO-2-naphthyl, ferrocenyl, 3-pyridyl, Bu

Scheme 19

The addition of dialkylphosphites to the double bond in styrene succeeded only for cyclic esters of phosphorous acid. It was found that the reaction catalysed with a rhodium complex gave the β-addition product, whereas the one catalysed with a palladium complex resulted in the product of α-addition to the double bond (Scheme 20). However, the asymmetric version of this reaction gave encouraging but rather modest results.[52]



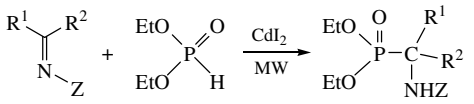
		β	α
RhCl(PPh$_3$)	85%	99	1
CpPd(allyl) / CyPMe$_2$	84%	6	94

NMDPP	JOSIPHOS	(*R*,*S*)-JOSIPHOS
β:α = 7:93	β:α = 67:33	β:α = 7:93
ee 2% (–)	ee 39% (–)	ee 56% (–)

Scheme 20

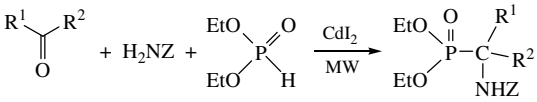
It is well known that the addition of dialkylphosphites to an unsaturated bond readily occurs in the case of carbonyl compounds and their nitrogen analogues, such as azamethines. We carried out the reaction of imines with dialkylphosphites (Pudovik reaction) and its trimolecular version, *viz.*, carbonyl compound–amine–dialkylphosphite (Kabachnik–Fields reaction) under microwave assistance and catalysis with a Lewis acid (CdI_2) (Scheme 21).

These conditions made it possible not only to shorten the reaction times considerably (from hours[53] to a few minutes or, sometimes, seconds) but also to perform the process with the carbonyl derivatives of natural porphyrins (Scheme 22); both



R^1 = Et, Pr, Ph
R^2 = H (45–90 s, 89–95%)
Z = Bu^t, Ph, Ph(Me)CH, cyclo-C$_6$H$_{11}$

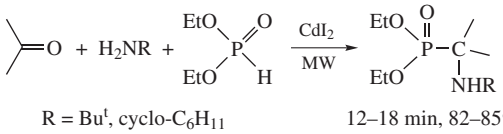
$R^1 + R^2 = (CH_2)_n$, n = 4, 5
Z = Ph(Me)CH, cyclo-C$_6$H$_{11}$ (1.5–10 min, 86–94%)



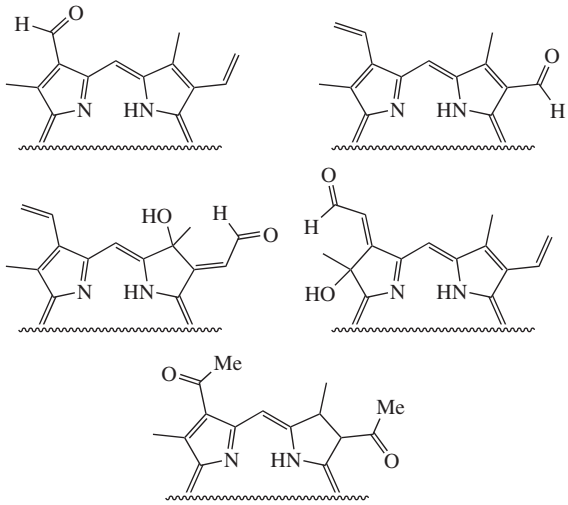
$R^1 + R^2 = (CH_2)_n$, n = 4, 5
R^1 = Pr^i, Ph, Me
R^2 = Pr^i, α-naphthyl, Ph, Me (10–25 min, 72–92%)
Z = cyclo-C$_6$H$_{11}$, Bu^t, Bn

Scheme 21

the latter and products of their conversions do not withstand prolonged heating.[54,55]

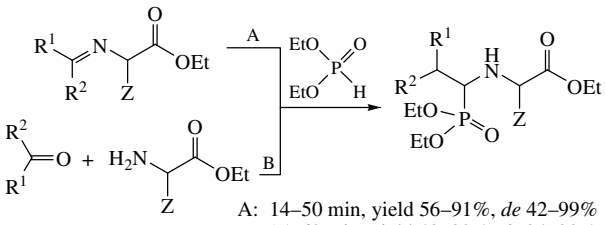


R = Bu^t, cyclo-C$_6$H$_{11}$ 12–18 min, 82–85%



Scheme 22

Among interactions of diethylphosphite with imines formed from α-amino acids, we found an example where the product (an α-aminophosphonate containing an alanine fragment) was formed with a high, almost quantitative diastereoselectivity (~100%). It should be noted that the value of *de* obtained in the stepwise reaction is higher than that in the trimolecular process (Scheme 23).[56]

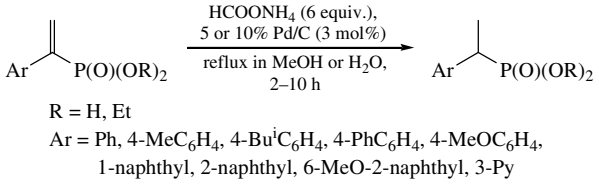


A: 14–50 min, yield 56–91%, *de* 42–99%
B: 15–60 min, yield 48–80%, *de* 34–88%
Z = H, Me, CH$_2$Ph
R^1 = H, Me, Ph,
R^2 = Et, Pr^i, Ph, 5-methyl-2-thienyl, 5-methyl-2-furyl
$R^1 + R^2 = (CH_2)_n$, n = 4, 5

Scheme 23

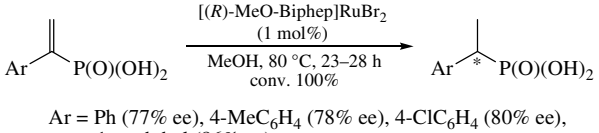
Preparation of α-aryl, α-amino and α-hydroxyphosphonates by the hydrogenation of unsaturated phosphorus derivatives

Interest in aryl-substituted ethylphosphonates and α-hydroxy-(α-amino)phosphonates stems from their biological activity (Ca^{2+}-antagonistic, neuroprotective, psychotropic, antibacterial and antiviral activities).[2,57–59] Phosphonates of this type can be obtained by the catalytic reduction of corresponding unsaturated organophosphorus precursors, such as alkenyl-, α-keto- or aryliminophosphonates. For example, α-(aryl)vinylphosphonates can be reduced to give P-analogues of known drugs, such as Naproxen and Ibuprofen. We have shown that this reduction readily occurs under Pd/C catalysis in the case of the reaction with hydride transfer, as well as on palladium deposited onto modified chitosan in the case of reduction with molecular hydrogen. In the latter case, we were able to recycle the catalyst without losing the catalytic activity (Scheme 24).[60]



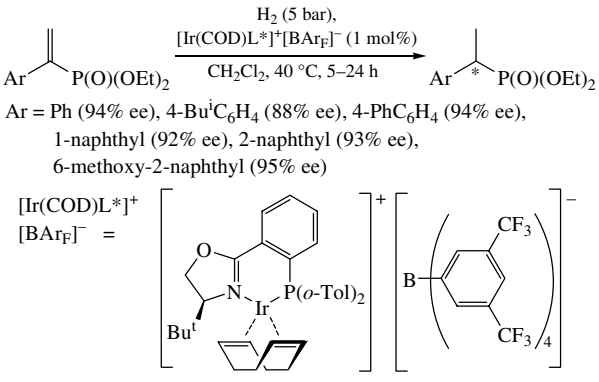
Scheme 24

We succeeded in performing asymmetric reduction using catalysis with ruthenium complexes containing chiral ligands; of these, (R)-MeO-Biphep was found to be the best (Scheme 25).[61]



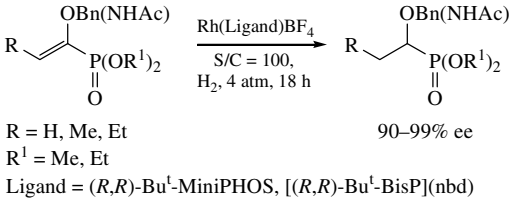
Scheme 25

However, the highest optical yields were reached with a phosphine-oxazoline cationic iridium complex (Pflatz catalyst) (Scheme 26). Note that the enantiomeric purity was as high as 95% for the P-analogue of Naproxen.[62,63]



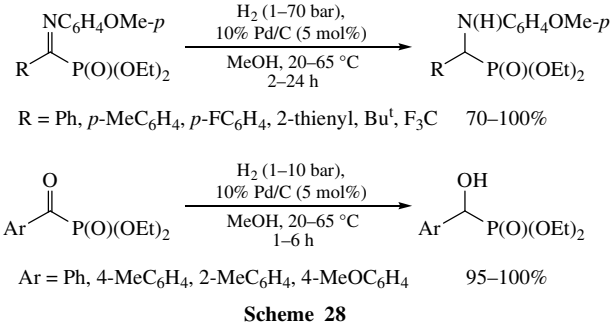
Scheme 26

Although the Rh-catalysed reduction of α-amino- and α-benzyloxyvinylphosphonates involving chiral ligands with an asymmetric centre on the phosphorus atom (Imamoto ligands) gave excellent results and the corresponding α-amino- and α-hydroxyphosphonates can be synthesised with high enantiomeric purity, this reaction is limited to compounds capable of enolisation, *i.e.*, it is not applicable to aryl (or trifluoromethyl) derivatives (Scheme 27).[64]



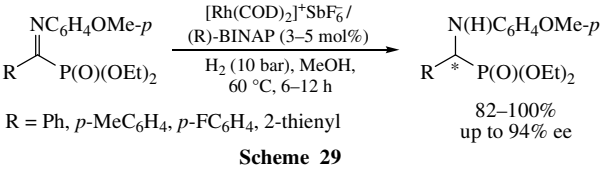
Scheme 27

We tried to carry out the asymmetric reduction of α-aryliminophosphonates and α-aryloxophosphonates using chiral rhodium complexes. The reduction of these compounds with molecular hydrogen catalysed with Pd/C occurs in high yield (Scheme 28).[65]



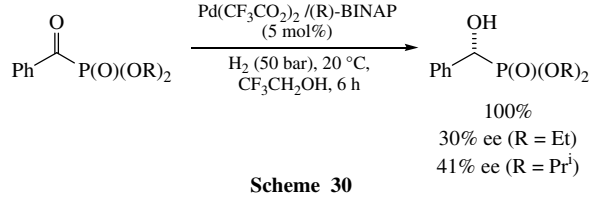
Scheme 28

However, it was found to be much more difficult to perform the asymmetric version of these reactions. Of many chiral ligands, it was only (R)-BINAP (R = *p*-MeC_6H_4) that gave 94% ee (Scheme 29).[66]



Scheme 29

Catalytic system $Pd(OAc_F)_2$–CF_3CH_2OH (50 atm, 20 °C) was found to be the best in the reduction of α-oxophosphonates, but the use of various chiral ligands, including (R)-BINAP, gave only meager results: α-hydroxyphosphonates were obtained with optical purity up to 41% (Scheme 30).

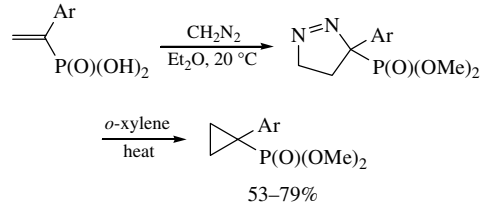


Scheme 30

Carbene chemistry for the synthesis of biologically active phosphonates

The α-arylvinylphosphonates obtained react with diazomethane to give α-arylcyclopropylphosphonates, an interesting class of organophosphorus compounds of prospective biological activities (Scheme 31).[67]

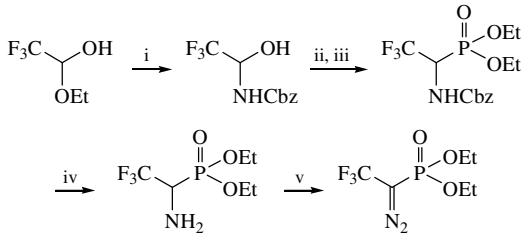
It is well known that the enhancement of the biological activity of organophosphorus compounds is caused by the presence of a CF_3 group in the α-position with respect to the phosphorus atom. In view of this, we synthesised a hitherto



Ar = Ph, 4-ClC_6H_4, 4-$Bu^iC_6H_4$, 4-PhC_6H_4, 2-naphthyl

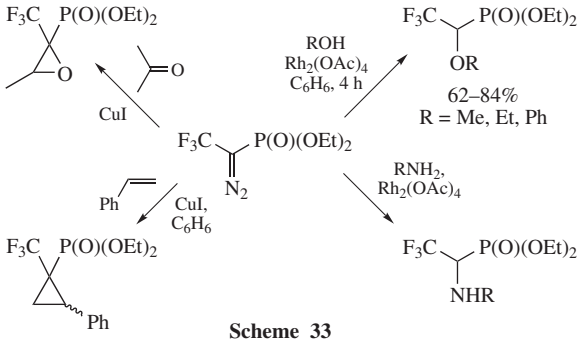
Scheme 31

unknown diazotrifluoromethylphosphonate, a source of a new carbene (Scheme 32).[68]



Scheme 32 *Reagents and conditions*: i, Cbz-NH_2, CH_2Cl_2, Et_3N, molecular sieves (5 Å), room temperature, 88%; ii, $(CF_3CO)_2O$, Py, iii, $HP(O)(OEt)_2$, Me_3SiCl, –20 °C, 84%; iv, H_2, Pd/C, MeOH, room temperature, 12 h, 100%; v, Pr^iONO, $CHCl_3$, 30 min, 67%.

A series of catalytic reactions of diazotrifluoromethylphosphonate has been carried out to produce diverse functionally substituted phosphonates (Scheme 33). Note that CuI was a more efficient cyclopropanation catalyst than rhodium complexes.



Scheme 33

Thus, catalytic methods for the synthesis and conversion of organophosphorus compounds not only expand considerably the knowledge of the chemistry of these compounds but also make it possible to synthesise a wide range of biologically active products.

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