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The review discusses recent achievements in the development of more environmentally friendly and economically competitive processes for the synthesis of biologically and synthetically important phosphorus-bearing compounds by conjugate addition of hydrogen-phosphonates to different Michael acceptors.

In memory of my teacher academician Mikhail Voronkov.

Introduction

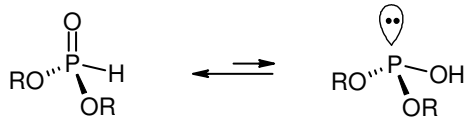
The carbon-heteroatom bond formation is the fundamental reaction in organic chemistry and materials science. One of the classical approaches for its construction is to be found in the conjugate addition of nucleophiles to electron-deficient alkenes, which is commonly known as hetero-Michael reaction. The use of various Michael donors allows the construction of different carbon-heteroatom bonds. Actually, the oxa-,[1] sulfa-,[2,3] seleno-,[3] aza-,[4] and phospha-[5] Michael additions seems to be the most widely applied in contemporary organic synthesis. It is not surprising because these processes are characterized as an atom-efficient way to many diversely functionalized products starting from inexpensive, simple and easily available starting materials.

Among these reactions the phospha-Michael addition is the intensively developed field and attracts much attention of the synthetic chemists in recent years.6 The reason for this is the fact that phosphorus-bearing compounds found a wide range of applications in agricultural, medicinal, technical and synthetic chemistry.7 Moreover, the direct addition of the nucleophilic element–hydrogen moiety to unsaturated carbon-carbon bond is the most straightforward and environmentally friendly chemical transformation.8

In fact, the amounts of the environmental pollution from chemical and pharmaceutical manufactories often several times higher than the amounts of useful product.[9] Clearly, the application of "clean" green technology is actually the challenge of our life. What progress in the field of phospha-Michael addition was achieved in the beginning of 21st century? What new catalytic systems were designed for this reaction? What efficient green and sustainable synthetic protocols were developed for the last decade? This review is focused in the reactions of alkenes activated by different functions - alkoxycarbonyl-, cyano-, carbonyl-, formyl- and nitro groups - with some phosphorus-centered nucleophiles.

Dialkyl- and diaryl H-phosphonates and thiophosphonates were selected as the model for phosphorus reagents containing the P(X)H moieties which are generally considered as poor nucleophiles. Their low reactivity often renders their applications and needs an efficient catalysts for the reaction to proceed under mild conditions and in an reasonable yield and selectivity. Moreover, often hydrogen phosphonate derivatives are versatile building blocks in the synthesis of diverse biologically important phosphonates and their analogs.[10] That is why, the study of the reaction of H-phosphonates with different Michael acceptors have attracted particular interest to synthetic chemists. Occasionally, the addition of H-phosphonates to activated unsaturated systems is also referred as the Pudovik reaction.[11]

The most important feature of H-phosphonates is that two tautomeric forms are possible in this case - phosphonate (**A**) and phosphite (**B**).[7,10,12]



A phosphonate form (non-nucleophilic)

B phosphite form (nucleophilic)

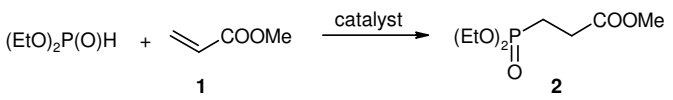
Evidently, the presence of a lone electron pair on the phosphorus atom of phosphite tautomer allows these compounds react readily as nucleophilic species. It is well known that the tautomeric equilibrium in solutions is almost completely shifted toward the former one but it can be shifted to the phosphite tautomer by appropriate catalysts, for example, Lewis bases and acids. On the other hand, Lewis and Brønsted acids can be used for the activation of Michael acceptor.

Unsaturated esters, amides and nitriles

The phospha-Michael addition of H-phosphonates to unsaturated acid derivatives as the initial substrates - esters, amides and nitriles - is widely documented in literature. Numerous research reports show that the effectiveness of this reaction depends strongly on both the structure of Michael acceptor, nature of the substituents at the phosphorus center and reaction conditions. This is perfectly illustrated by the following examples. It was reported that the addition of dimethyl- or diethyl phosphonates to acrylamide proceeded smoothly in the presence of strong organic bases (such as DBU) giving rise to the anti-Markovnikov adduct in good yield. In contrast, the attempts to apply the same conditions for the reaction of the same nucleophiles with acrylonitrile failed. In this case the reaction was successfully promoted when new catalytic system containing KOH supported on Al_2O_3 was used.[13] In another example, dimethyl thiophosphonate was added readily to acrylonitrile or *tert*-butylacrylate at room temperature without any catalyst,[14] but the reaction of 2-chloroacrylonitrile with dialkyl phosphonates occurred exclusively under catalytic conditions.[15] So, it is clear that the significant efforts of chemical community are directed toward the development of efficient green methodology, in particular, where the reactions proceed under the action of a low amount of catalyst (recyclable and reusable catalysts are preferred) and in non-toxic solvents (or without using any solvent at all).

Usually, the phospha-Michael addition is base-catalyzed process. A number of catalysts (sometimes, conceptually new) are being developed for the last decades. Highly basic nonnucleophilic nitrogen derivatives and some inorganic compounds were found to be the most effective catalysts for this reaction. The best results were obtained with DBU,[16] DABCO,[17] BSA,[18] TBD,[19] aliphatic amines,[20,21] guanidine derivatives,[19,22] metal oxide, [23,24] alkali metal hydroxides[13] and carbonates.[25]

Thus, no reaction occurs when methyl acrylate **1** is treated with diethyl phosphonate at the presence of solid MgO, Na_2CO_3 or polymer-supported sodium carbonate.[23] However, the same nucleophile ready undergoes a conjugate addition to ester **1** even at room temperature when DBU [16] or CaO [23] are used as catalyst (Scheme 1). It is remarkable that eco-friendly and inexpensive calcium oxide show the same effectiveness that strong organic bases. The requirement of its stoichiometric amount seems to be the only one disadvantage of reported method.



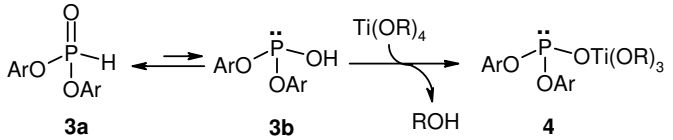
catalyst = DBU (70%), CaO (80%)

Scheme 1. Reaction of methyl acrylate with diethyl phosphonate

Besides organic and mineral bases, the 1,4-conjugate addition of dialkyl phosphonates to unsaturated esters and nitriles is commonly promoted by certain Lewis and Brønsted acids such as $AlMe_3$,[26,27] $Ti(OPr^i)_4$,[28] $HClO_4/SiO_2$.[29] Moreover, these methods are more attractive because of mild reaction conditions, reasonable yield and short reaction time.

Importantly, the use of $AlMe_3$ as a catalyst allows to introduce into the reaction α-mono- or β,β-disubstituted esters. It is well know that the conjugate nucleophilic addition to β,β-disubstituted activated alkenes leading to the generation of quaternary center remains one of the challenging problems of contemporary organic synthesis. For aza-Michael reaction the same difficulty was successfully overcome recently. It was found that addition of secondary amines to α,β- and β,β-disubstituted Michael acceptors occurs under high pressure (up to 16 kbar) in absence of any catalyst.[30,31] But reports on the creation of the quaternary phospha-carbon center are yet rare.

As it was mentioned before, the effectiveness of the reaction depends on the nature of substituents at the phosphorus atom. It is recognized for a long time that the reaction conditions optimized for dialkyl phosphonates often fail for their diaryl substituted analogues. For example, although traditional Lewis bases (Et_3N, DBU) and acids ($AlCl_3$, $TiCl_4$) successfully catalyzed the addition of dialkyl phosphonates to methyl acrylate, these catalysts were absolutely ineffective when diphenyl phosphonate were used in the same reaction. Yao assumed that transesterification of the initial H-phosphonate with $Ti(OPr^i)_4$ should merely shift the equilibrium of two tautomeric forms **3a** and **3b** toward more active metalloxy phosphite **4** and therefore to favor the nucleophilic addition (Scheme 2). This hypothesis was perfectly confirmed when a variety of substituted acrylates were treated with $(PhO)_2P(O)H$ in the presence of catalytic amount of $Ti(OPr^i)_4$. In these cases the target γ-oxophosphonates were obtained in quantitative yield.[28] Early the similar modifications of dialkyl phosphonates into trimethylsiloxy phosphorus (III) derivatives by using TMSCl instead of $Ti(OPr^i)_4$ were proposed by Afarinkia and co-workers.[15]

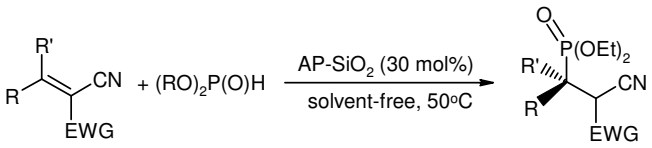


Scheme 2. Transesterification of diphenyl phosphate **3**

For last years the use of catalysts affixed to polymer or mineral support became increasingly popular. In fact, heterogenization of homogeneous catalyst by its incorporation onto insoluble support material simplifies the experimental procedure, ensures

carrying out reaction under solvent-free conditions and minimizes the amount of waste. In this case the catalyst is easily recovered after reaction and often can be recycled for several times without loss of activity. Sometimes, the catalytic activity of such systems is higher and, as a consequence, the reaction time is significantly decreased. Moreover, there are the examples where the reactions occur only at the presence of supported catalyst. Silica gel [29, 32] and alumina [13,33] are most popular as a support material.

For example, the system KF/Al_2O_3 is known for a long time as an efficient and convenient catalyst for different carbo- and hetero-Michael addition reactions, including the addition of dialkyl phosphonates to α,β-unsaturated carbonyl derivatives.[33] The aminopropylated silica gel was proposed as an efficient and reusable heterogeneous catalyst for addition of dialkyl phosphonates to various type of alkylidene and arylidene malonate-type derivatives under solvent-free conditions (Scheme 3).[32] It is very important to note that this method is applicable for the reaction with β,β-disubstituted malonates and some β-monosubstituted Michael acceptors bearing different electron withdrawing groups (for example, ethoxycarbonyl and cyano functions). At the same time others activated alkenes such as ethyl benzylidenemalonate, nitrostyrene and even acrylonitrile failed to react: no products were isolated in these cases.



EWG = CN, COOEt

R' = H; R = Ph, 4-MeC_6H_4, 3-$MeOC_6H_4$, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-HOC_6H_4, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$, 2-naphthyl, 2-furyl, 2-thienyl, 2-pyridyl

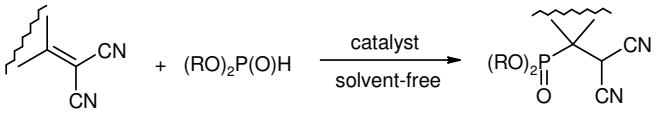
R' = Et, R = Me; R',R = 

Scheme 3. Addition of dialkyl phosphonates to unsaturated malonates.

The extensive research in nanotechnology gave impetus to the application of nano catalysts in different types of catalytic reactions. Impressive results were recently obtained by Hosseini-Sarvari and co-workers who developed an efficient, mild and rapid green protocol to generate carbon – phosphorus bond.[34,35] They have shown that nanosized metal oxides (especially, ZnO) exhibit excellent performance in the conjugate addition of diethyl phosphonate to arylidene malonate derivatives (Scheme 4). The target adducts were produced in quantitative or almost quantitative yields under solvent-free conditions and room temperature for a short reaction time (mostly, 0.5 – 3 h). In contrast, when the reactions carried out in solvents the target phosphonates were obtained in moderate yields even during longer reaction time. No reaction occurred in the absence of catalyst. It should be strongly emphasized that nanosized prepared zinc oxide was much more effective that commercially available ZnO. Moreover, the catalytical activity depended on the morphology of nanoparticles: nano-rods ZnO was found to be much more effective than nano-flakes one. The reaction mechanism of catalyst action is still ambiguous. The authors explained this phenomenon in terms of specific surface area and size of nanoparticles of the catalyst.

Very recently excellent results were obtained when the same reaction was catalyzed by iron-doped single walled carbon nanotubes (Fe/SWCNTs).[36] The catalyst's activity was retained unchanged even after 10 reaction cycles (Scheme 4).

Because the heterogeneous catalyzed reaction occurs at the surface of catalyst, the great efforts were made to increase the surface area by distributing it over the nanomaterial support. This approach was successfully tested with a nano γ-Fe_2O_3-pyridine based catalyst which was used for the reaction of diethyl phosphonate with unsaturated malonate derivatives.[37] The reactions completed in few minutes at room temperature leading to the target adduct with high yield.



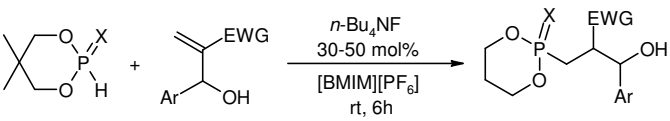
Scheme 4. Nano catalysts in the phospha-Michael addition of dialkyl phosphonates.

entry	catalyst	R	conditions	yield, %	examples	ref.
1	Fe/SWCNTs, (5 mol%)	Et	50°C, 2.5-6.5 h	85-95	10	36
2	nano-flakes ZnO, (5 mol%)	Et	50°C, 0.5-10 h	98	10	35
3*	nano-rods ZnO, (10 mol%)	Me, Et, Ph	rt, 0.75-3 h	88-98	9	34

* Initial alkenes were generated *in situ* from isatin and malononitrile.

Table 1. Nano catalysts in the phospha-Michael addition of dialkyl phosphonates.

Ionic liquids (IL) often considered as green chemistry solvents both in laboratory practice and industry. Sometimes, they were used at the same time as convenient solvents and highly efficient catalytic systems. The example of the phospha-Michael reaction in popular ionic liquid $[BMIM][PF_6]$ is depicted in Scheme 5.



yield 72-84%
9 examples

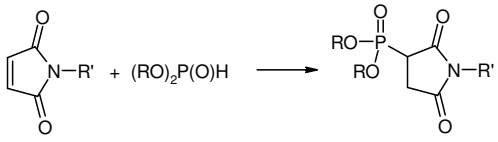
X = O, S; EWG = COOMe, CN

Ar = Ph, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$, 1-furfuryl

Scheme 5. Addition of cyclic H-phosphonates in IL.

The authors frankly noted that the best results they obtained when DMF was used as a solvent. However, IL offer a remarkable advantage due to the fact that they can be easy recovered and reused in the same reaction at least twice.[38]

Finally, a non-classical method of activation of phospha-Michael reaction by microwave radiation (MW) is worthy to note.[39] The successful application of MW to perform the phospha-Michael reaction was reported recently (Scheme 6).[38]



R = Me, Et [38], Ph [17];
R' = Me, Ph [38], Ph, Bn, 4-MeC_6H_4, 4-$MeOC_6H_4$ [17]

reaction conditions:
MW, solvent-free,175°C, 2.5 - 3 h; yield 71-95% [38]
TBD (20 mol%), toluene, rt, 5 min; yield 78-94% [17]

Scheme 6. Addition of H-phosphonates to maleic derivatives.

It was shown that microwave assisted addition of dialkyl phosphonates to maleic derivatives (amide or anhydride) was faster than under the classical thermal conditions. Moreover, there is no need for a solvent and catalyst under the MW activation. However, this method seems to be of little use because the alternative catalytic approach is now preferred due to simple procedure, short reaction time and low temperature.[19]

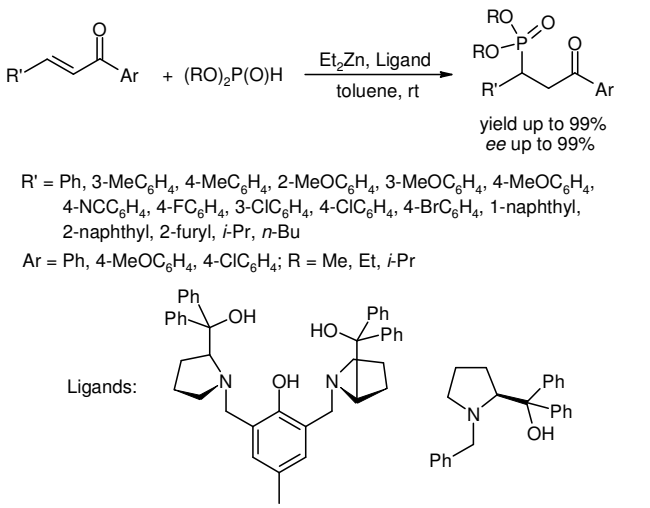
Enones and enals

The molecules of enones and enals represent a class of poly-electrophiles which can participate in two competitive 1,2- and 1,4-addition pathways. The former opens the direct access to α-hydroxyphosphonates, the latter leads to phospha-Michael adduct.

Like unsaturated esters, amides and nitriles considered above, enones mainly react with dialkyl- and diaryl phosphonates in the presence of basic catalysts. Usually, among these Michael acceptors terminal (methylvinylketone) and cyclic (cyclopentenone, cyclohexenone) enones were used. β,β-Disubstituted enones were absolutely inert in the reaction with both diehyl-, diphenyl- or di(trifluoro)ethyl phosphonates.[41]

Because the chiral phosphonates are attractive biologically active compounds, a considerable attention of synthetic chemists was paid to stereoselective synthesis of these derivatives. The first catalytic asymmetric 1,4-addition of diethyl phosphonate to acyclic enones leading to γ-oxophosphonates in high yields and with excellent enantioselectivities was described by Wang and co-workers (Scheme 7).[42]

The first example of successful phospha-Michael addition of the same H-phosphonate to chalcones catalyzed by lanthanide complexes was disclosed very recently by Shen and co-workers.[43] During the catalysts screening process, the authors found that the reaction exhibited impressive product selectivity as a function of the catalyst nature.

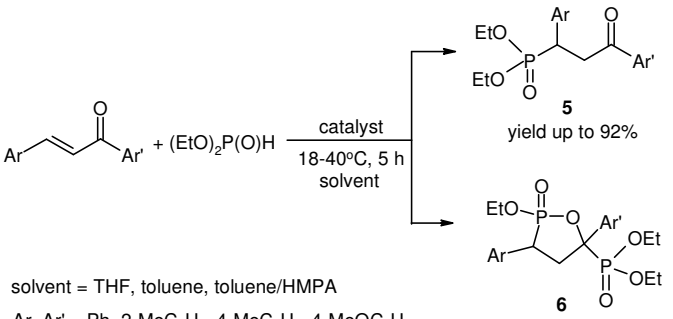


R' = Ph, 3-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-FC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 1-naphthyl, 2-naphthyl, 2-furyl, *i*-Pr, *n*-Bu

Ar = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4; R = Me, Et, *i*-Pr

Scheme 7. Enantioselective synthesis of γ-oxophosphonates.

The best results were obtained when the complex of lanthanide having a small ionic radius and high Lewis acidity were used. Increasing the ion size from Yt to La led to the decrease of the yield of phospha-Michael adduct **5** due to the gradual increase in the yield of Michael/Pudovik reaction product **6** (Scheme 8). So, the suggested protocol allowed to synthesize the target organophosphorus compounds in good yields and selectivity.



solvent = THF, toluene, toluene/HMPA

Ar, Ar' = Ph, 2-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 4-$Me_2NC_6H_4$, 1-naphthyl

catalyst = $Yb(OAr)_3(THF)_2$, $Nd(OAr)_3(THF)_2$, $La(OAr)_3(THF)_2$, $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$, $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, NaOAr, $Li[N(TMS)_2]$

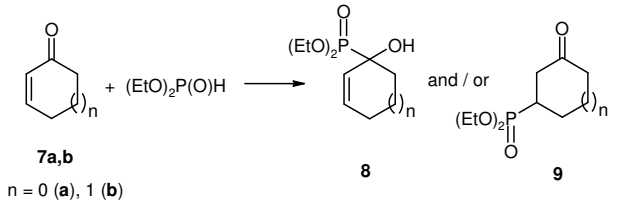
Scheme 8. Dependence of regioselectivity on the catalyst nature.

The most intriguing problem of the reactions of dialkyl- and diaryl phosphionates with enones and enals seems to be a selectivity of nucleophilic attack, *i.e.* the competition between 1,2- and 1,4-addition. When the conjugate addition to the carbon-carbon double bond and when reaction of the carbonyl group can be expected? A number of both unambiguous and contradicted results were reported over the past few years.

The majority of obtained results demonstrated that in many examples the relatively trivial changes in the solvent, temperature, nature of catalyst and even its amounts (!), finally, in the structure of initial unsaturated carbonyl derivative and H-phosphonate dramatically affects the reaction direction. This fact of course adds the difficulties to researchers working in this

field of organic synthesis but also give the charm and fascination to this chemistry.

Some representative examples are depicted in Scheme 9. Thus, the only 1,2-addition product **8** was isolated when diethyl phosphonate was treated with 2-cyclopenten-1-one **7a** in the presence of CaO (Table 2, entries 3, 4).[23]



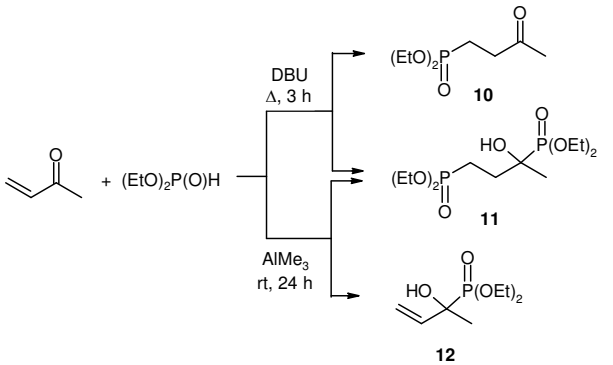
Scheme 9. Dependence of regioselectivity on the catalyst nature and structure of enone.

entry	n	catalyst	solvent	product	yield, %	ref.
1	0	Ln-complex	toluene	**9**	84	45
2	1	Ln-complex	toluene	**8**	86	45
3	0	CaO	neat	**8**	67	23
4	1	CaO	neat	**8**	78	23
5	0	EtONa	EtOH	**9**	42	44
6	1	*n*-Bu_3P	MeCN	**8 + 9**	5 + 66	46

Table 2. Dependence of regioselectivity on the catalyst nature and structure of enone.

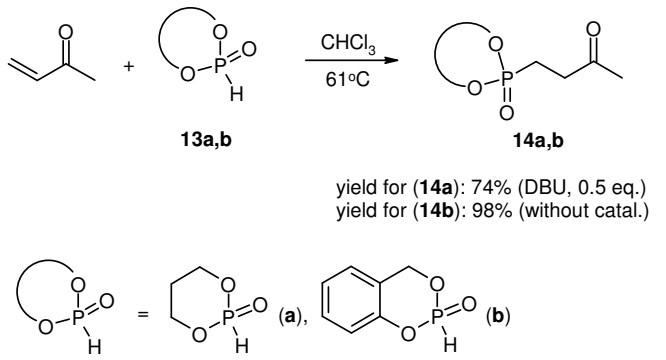
In contrast, when ethoxide of sodium[44] or lanthanide amido complexes[45] were used as catalysts the 1,4-adduct **9** was obtained exclusively. Finally, both 1,2- (5%) and 1,4-adducts (66%) were isolated when the same reaction was carried out at the presence of *n*-Bu_3P (10 mol %).[46] The use of 2-cyclohexen-1-one **7b** instead of its five-membered ring analogue **7a** leads sometimes to the opposite results (Table 2, entries 1, 3, 5).

The outcome of the reaction of non-cyclic enones such as methylvinylketone with diethyl phosphonate was shown to be dramatically dependent not only on the nature of catalyst but also its quantities.[44] Thus, a 22:78 mixture of bis-adduct **11** and α-hydroxyphosphonate **12** was formed in the presence of $AlMe_3$ as catalyst while an 89:11 mixture of 1,4- (**10**) and bis-adducts (**11**) was obtained when reaction was catalyzed by DBU (0.5 equiv.). The decreasing of amount of catalyst led to a conversion decreasing, but its increasing up to 1.0 equiv. gave the complex reaction mixture containing only 60% of the target compound **10** (Scheme 10).



Scheme 10. Regioselectivity of addition to methylvinylketone.

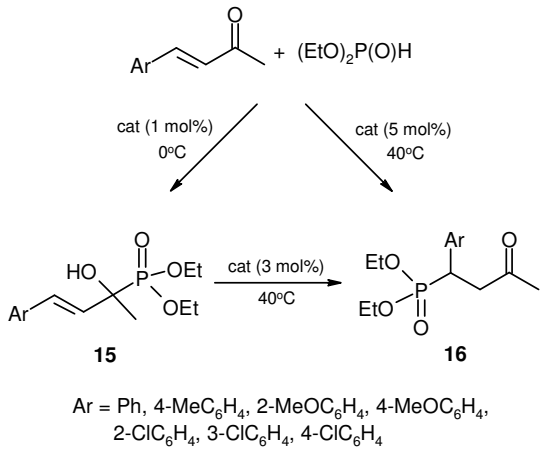
Interestingly that phospha-Michael addition of heterocyclic H-phophonates can proceed as non-catalytic process. For example, DBU (0.5 equiv.) was required for the reaction of methylvinylketone with H-phosphonate **13a**, while the addition of its homologue **13b** to the same Michael acceptor could be carried out without any catalyst leading to phosphonate **14b** in quantitative yield (Scheme 11).[47]



Scheme 11. Addition of heterocyclic H-phosphonates to methylvinylketone.

Last year a highly chemo- (100% of 1,2-adduct) and enantioselective (ee up to 99%) methodology of 1,2-hydrophosphonylation of β-aryl substituted enones with dialkyl phosphonates was proposed.[48] The reaction proceeded at lowering temperature and catalyzed by chiral magnesium (II) binaphtolate aqua complexes as cooperative Brønsted/Lewis acid-base catalysis.

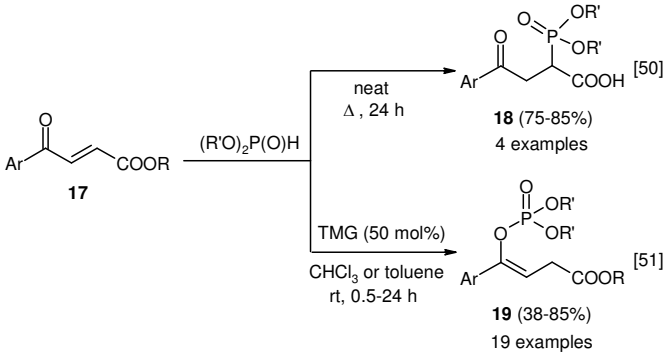
It is quite probable that such results could be explained not only by nature of catalysis but the reaction conditions. In fact, the critical dependence of the type of product on the reaction temperature was shown more than 15 years ago.[49] Recently, this effect was confirmed on the catalytic addition of diethyl phosphonate to substituted benzylideneacetone (Scheme 12).[45] Only 1,2-adducts **15** were obtained when the reactions were run at 0°C, while 1,4-addition product **16** was isolated when the same reactions were carried out at 40°C or higher temperature.



Scheme 12. Catalytic addition of $(EtO)_2P(O)H$ to benzylideneacetones and isomerization of 1,2-adduct into 1,4-adduct.

But more interesting that the authors shown that 1,2-adducts **15** could be transformed to 1,4-adducts **16** at elevating temperature (~40°C) in the presence of the same catalyst. It should be also noted that the neutral pyrrole supported rare-earth complexes prepared and described by Wang are the most active catalytic system for addition of H-phosphonates to α,β-unsaturated carbonyl compounds (enals, enones, esters, amides).

When the second electron-withdrawing group EWG was introduced into the molecule of electron-deficient alkene, another type of selective addition should be regarded. Evidently, the regioselectivity of addition in this case depends on the acceptor ability of both functional groups. It is reasonable to suggest that the introduction of the second electron withdrawing group lead to the increasing of the electrophilicity of olefinic carbon atom. In fact, such "twice activated" (so-called pull-pull) alkenes are more reactive, and their reactions with H-phosphonates sometimes occur without any catalyst. For example, the reaction of dimethyl- or diethyl phophonates with 4-oxo-enoate **17** (R = H) proceeds efficiently under heat for 24 h with the absence of catalyst to give γ-oxophosphonate **18** (Scheme 13).[50] Recently, Xiao and co-workers re-examined this reaction in the presence of organic base (TMG) and found that in sharp contrast to the previous communication, this reaction gave rise to the enol phosphates **19**.[51] According to the authors, the most probable pathway of its generation includes the phospha-Michael addition/intra-molecular cyclization/rearrangement sequence. The similar sequence of transformations were observed when 4-ethoxy substituted CF_3-enone was treated with diethyl phosphonate.[52]



Scheme 13. Reactions of 4-oxo enoates **17** with H-phosphonates.

The reactions of enals with dialkyl phosphonates are usually regarded as effective routes to the α-hydroxy phosphonates or products of their further transformations. In fact, there have been many reports on the 1,2-addition of H-phosphonates to unsaturated aldehydes. Recently, a comprehensive review on the environmentally friendly syntheses of α-substituted phosphonates was published.[53] The structure of enals did not affect the reaction direction: 1,2-addition observed with both captodative systems[54-57] and α-halogenenals[58] having highly electrophilic β-carbon atom[59] or even terminal enals.[60] Interestingly, the poly-electrophiles bearing simultaneously three functional groups - a carbon-carbon double and triple bond and formyl group - react with dialkyl phosphonates leading to only α-hydroxy phosphonates.[61] The products of competitive 1,4-addition were formed only in negligible amounts or were not observed at all.

In this context it was surprisingly to find an example where the only chemoselective 1,4-addition to enals occurs. Trautmann and co-workers reported that some Michael acceptors including 2-butenal reacted with dimethyl thiophosphonate to afford β-substituted phosphonothionate in excellent yield.[14] The reaction proceeded smoothly at room temperature without any catalyst (Scheme 14).

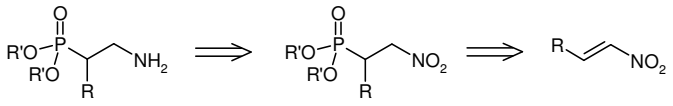
Scheme 14. Reactions of 2-butenal with dimethyl thiophosphonate.

Interestingly, the same aldehyde reacted selectively with dimethyl phosphonate at the presence of either Lewis bases or Lewis acids affording corresponding α-hydroxyphosphonate in high yield.[62,63]

Nitroalkenes

Nitroalkenes are interesting Michael acceptors particularly due to the synthetic versatility of the nitro group. The phospha-Michael addition of H-phosphonates to nitroalkenes has received a great attention in the last decade. The synthesis of β-nitrophosphonates remains a considerable challenge owing to a broad spectrum of their biological activity and wide application in peptide and medicinal chemistry. In fact, these compounds serve value precursors for the β-amino phosphonic derivatives which can be regarded as non-proteinogenic phosphorus analogues of β-amino acids. Additionally, it is well known that these isosteres of aminoacids were found in nature.

One of the most elegant route to β-aminophosphonic acid derivatives is provided by the conjugate addition of dialkyl- and diaryl phosphonates to nitroalkenes followed by the reduction of nitro group to amino (Scheme 15).

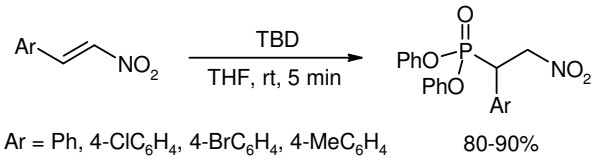


Scheme 15. Retro-synthetic scheme of preparation of β-aminophosphonic acid derivatives.

The first example of the addition of H-phosphonates to nitroalkenes was reported more than half a century ago.[64] The current efforts of chemical community are made in two principal directions. First, to achieve a decisive progress in the improvement of the procedure for generation of C-P bond in the reaction of nitroalkenes with H-phosphonates new methods were examined. Second, the search of catalytic systems for

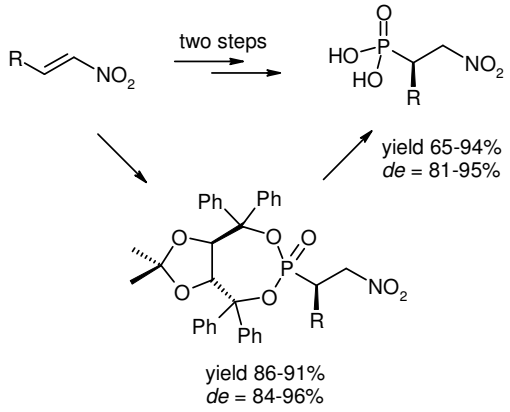
asymmetric hydrophosphorylation of activated double-double carbon bond was performed.

As in the series of α,β-unsaturated carbonyl derivatives, the reaction of nitroalkenes with H-phosphonates is the base-promoted process. The most successful catalyst was proposed by Tan's research group.[19] They developed a mild and rapid protocol for the reaction of nitrostyrenes with diphenyl phosphonate using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as superbase (Scheme 16). Nitroalkenes bearing either EWG or EDG in benzene ring were efficiently transformed into target adducts in high yield at room temperature within 5 minutes!



Scheme 16. Synthesis of β-nitrophosphonates.

Because of stereogenic center can be created in the course of the 1,4-conjugate addition reaction, much effort has been made to develop efficient catalytic enantioselective methods of β-nitrophosphonate preparation. Two highly efficient and practical approaches to chiral β-nitrophosphonate derivatives have developed over the last few years. One of them consists of using chiral H-phosphonates as nucleophiles. For the first time this methodology was applied by Enders's research group.[65,66] The authors reported that when aromatic nitroalkenes were treated with enantiomeric pure H-phosphonate, the phospha-Michael adducts were obtained in good yields and with high diastereoselectivity (Scheme 17). The further treatment of resulting phosphonates with TMSCl and NaI and following hydrolysis afforded corresponding β-nitrophosphonic acids practically without racemization.



R = Ph, 4-PhC6H4, 2,3,4-(MeO)3C6H2, 4-MeC6H4, 1-naphthyl, Fc

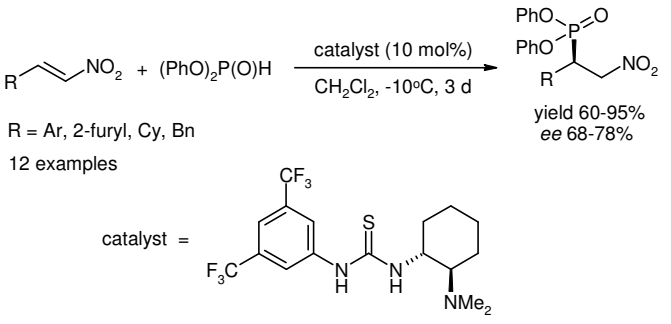
Scheme 17. Chiral H-phosphonates in the synthesis of β-nitrophosphonates.

The same procedure was also applied to aliphatic nitroalkenes. In this case, the target β-nitrophosphonic acids were obtained in good yield (85-95%) but, unfortunately, with unsatisfactory enantiomeric excess.

Latter, the authors successfully adopted this method to the synthesis of α,β-disubstituted β-nitrophosphonates bearing two new neighboring stereogenic centers.[66]

An alternative approach to just described is organocatalyzed pathway. The pioneer organocatalytic enantioselective phospha-Michael addition of H-phosphonates to nitroalkenes was reported almost simultaneously by Wang's [67] and Terada's [68] research groups. Thus, ten bifunctional organocatalysts, including *Cinchona* alkaloids, were screened for the 1,4-conjugate addition of aryl- and alkyl phosphonates to *trans*-β-nitrostyrenes.[67] The results shown a significant variety of activity studied catalytic systems. The best result was obtained when β-nitrostyrene was treated with $(PhO)_2P(O)H$. In this case the addition occurred rapidly (5 min) in good yield (88%) but with poor enantioselectivity (23%). When diethyl phosphonate was introduced in the same reaction, the target adduct was obtained in ~5% yield for 48 h without any enantioselectivity. Other nitrostyrenes underwent phospha-Michael reaction with diphenyl phosphonate in toluene at -55°C for 6 days afforded the adducts in moderate to good yields and selectivity. For the first time the enantioselective addition of dialkyl phosphonates to nitroalkenes was successfully carried out in the presence of heterobimetallic (*S*)-(-)-aluminum lithium bis(binaphthoxide) complex.[69]

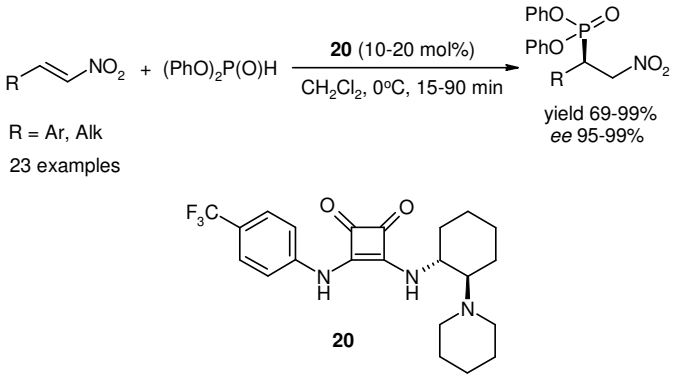
At the same time, Terada and co-workers developed a highly enantioselective version of 1,4-conjugate addition of diphenyl phosphonate to a broade range of nitroalkenes bearing either aromatic or aliphatic substituents. For this aim they applied axially chiral guanidines as efficient Brønsted base catalyst (Scheme 18). The target addition products were isolated in good to excellent yields (79-98%) and with high enantioselectivity (up to 97%).[68,70] Unfortunately, dialkyl phosphonates (dimethyl-, diisopropyl- and dibenzyl-) did not react under the same reaction conditions. The authors supposed that these results can be explained by the drastic variation of pK_a values of the initial H-phosphonates.



Scheme 18. Organocatalytic enantioselective pathway to β-nitrophosphonates.

A new family of chiral catalysts based on a squaramide scaffold was developed by Rawal and co-workers.[71] In fact, squaramides are considered as an emerging class of hydrogen-bonding catalysts owing to their unique structural features. A series of squaramide type catalysts were tested. The compound **20** was found to be the most efficient in the reaction of both aromatic and aliphatic nitroalkenes with diphenyl phosphonate (Scheme

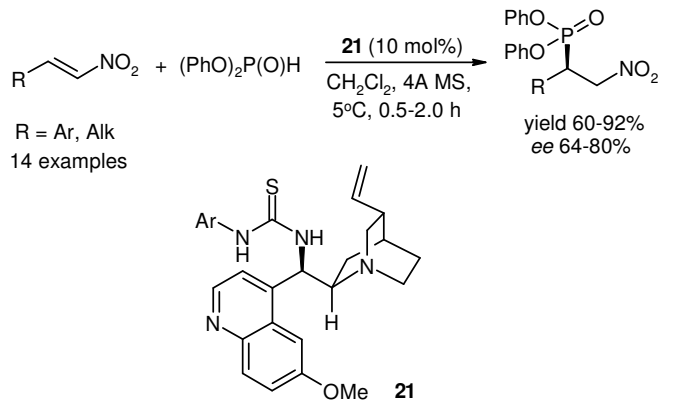
19). However, in the set of alkyl substituted substrates reactions were expected to be slower and the catalyst loading was increased from 10 to 20%. Remarkably, excellent results were obtained with sterically bulky aliphatic nitroalkenes, which are well known to be poorly reactive. For example, even highly hindered *tert*-butyl substituted substrate reacted with diphenyl phosphonate under optimized conditions affording the target adduct in 83% yield and with 96% enantiomeric excess.



Scheme 19. Enantioselective synthesis of β-nitrophosphonates.

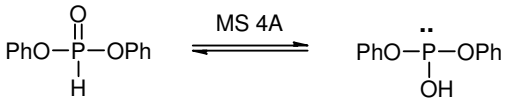
Further benefits of the use of thiourea derivatives were reported recently by Zhao's research group.[72] They reexamined the reaction of diphenyl phosphonate with *trans*-β-nitrostyrene and found that it can be dramatically improved by using molecular sieves (MS) as the additives (Scheme 20).

Thus, using readily available quinidine thiourea **21** as the catalyst in this reaction, the authors showed that the target β-nitrophosphonate was formed with good *ee* value (68-73%) but in a low yield (less than 42%). The addition into reaction mixture of molecular sieves slightly improved the enantioselectivity of the reaction (up to 84%) and significantly increased the yield of the adduct (up to 92%).



Scheme 20. Quinidine thiourea catalyzed enantioselective synthesis of β-nitrophosphonates.

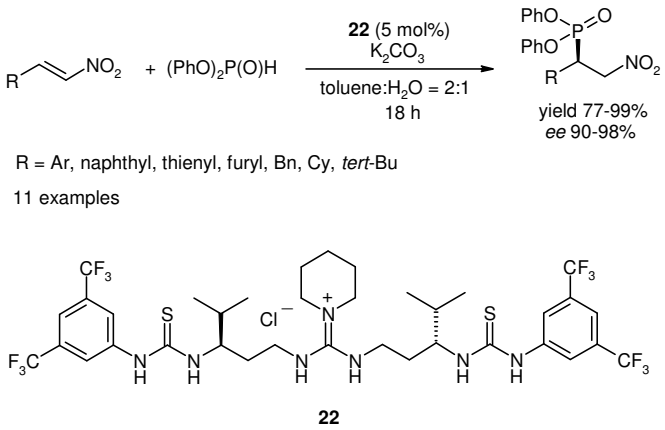
Evidently, molecular sieves played an especial role in the reaction. The authors hypothesized that as a heterogeneous Lewis acids MS influence on the equilibrium of two tautomeric forms of diphenyl phosphonate favoring to the formation of phosphite one (Scheme 21). Only phosphite form is well known to be reactive in phospha-Michael reaction (see Introduction). To verify this hypothesis the authors treated the commercially available diphenyl phosphonate by molecular sieves 4A for 0.5 h and after filtration registered ^{31}P NMR spectrum. Comparison of the spectra before and after the treatment allowed them to conclude that the concentration of phosphite form increases considerably.



Scheme 21. Molecular sieves influence on the tautomeric equilibrium.

A novel efficient organocatalyst bearing thiourea moiety was recently proposed by Sohtome and Nagasawa group.[73] It was shown that the conformationally flexible guanidinum/bisthiourea hydrochloride **22** catalyzed the phospha-Michael addition of diphenyl phosphonate to both aryl- and alkylnitroolefins leading to target adducts in high yield (77-99%) and with an excellent enantioselectivity (90-98%) (Scheme 22). This catalyst has some important advances: it can promote the reaction in a little amounts and displayed extraordinary catalytic activity with poorly reactive nitroalkenes. Thus, diphenyl phosphonate reacted with β-nitrostyrene even in the presence of 1 mol% of catalyst without any loss of both a reactivity (yield 99%) and enantioselectivity (*ee* 95%). The sterically bulky nitroalkenes bearing naphthyl-, cyclohexyl- and *tert*-butyl substituents were also available to add diphenyl phosphonate in high yield and selectivity.

In general, due to the procedure simplicity, efficiency and versatility, the methodologies developed over last few years on the base of bifuctional thioureas and squaramides seem to be the more utilizable in the synthesis of β-nitrophosphonates.



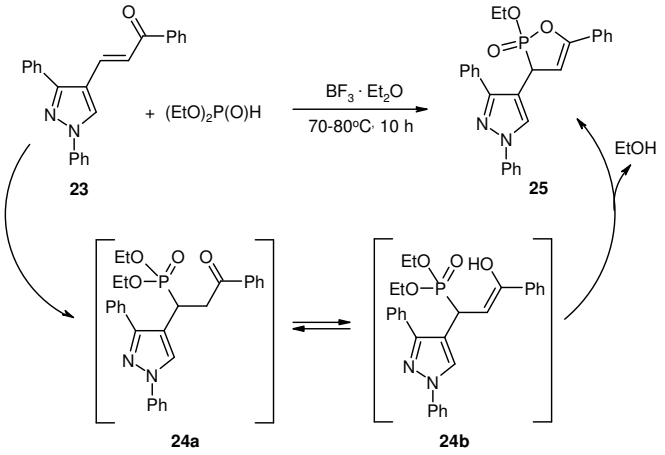
Scheme 22. Guanidinium/bisthiourea organocatalyst in enantioselective phospha-Michael addition to β-nitroolefins

Domino reactions including the Pudovik addition

Domino reactions were extensively developed over the last decades because they give access to complex molecules starting from simple reagents in one-pot procedure. This methodology

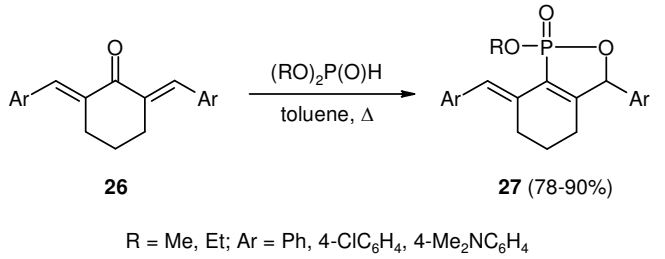
allows to reduce the amount of waste products and shorten the route to the target compounds. The only some representative striking transformations initiated by the phospha-Michael (Pudovik) reactions will be discussed here.

The oxaphosphole derivatives with the structures similar to that of phosphosugars are of particular interest. It is not surprising that many attempts of their synthesis were made for the last years. Recently, one-pot synthetic approach to the novel phosphorus heterocycles was reported.[74] The reaction of diethylphosphonate with chalcone **23** yielded phospha-Michael adduct **24a** which further underwent intramolecular cyclization under the same reaction conditions via tautomeric form **24b**. As a result, the oxaphospholylpyrazole **25** was isolated as a sole product. This multistep one-pot synthesis of derivatives containing the organophosphorus moiety associated with the important nitrogen-bearing nuclei is the efficient method of assembly of bioactive heterocyclic compounds (Scheme 23).



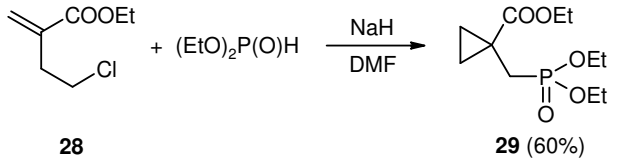
Scheme 23. Domino-synthesis of oxaphosphole derivatives via 1,4-addition mode.

Another easy and efficient cascade synthesis of such type of compounds from 2,6-bis(benzylidene)cyclohexanones and dialkylphosphonates was described by Boulos and co-workers.[75] The authors presume that in this case the reaction initiated by a nucleophilic attack of H-phosphonates on the carbonyl carbon of the initial substrate **26**. The intermediate 1,2-adduct underwent intramolecular cyclization followed by rearrangement and alcohol elimination to give finally oxaphosphole **27** (Scheme 24).



Scheme 24. Domino-synthesis of oxaphosphole derivatives via 1,2-addition mode.

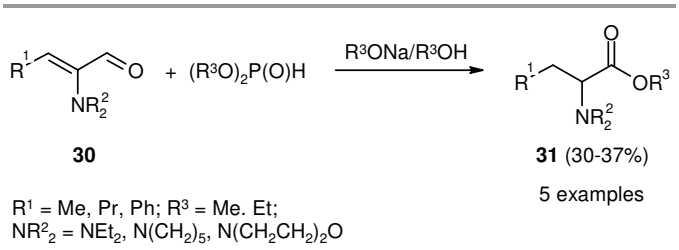
Recently, Beaudegnies and co-workers reported an efficient synthesis of cyclopropane ester derivatives by Michael addition-induced ring-closure reaction.[76] When ethyl-2-(2-chloroethyl)acrylate **28** was treated with carbon- or heteroatom-centered nucleophiles, including diethylphosphonate, the functionalized cyclopropane esters were isolated in high yield (Scheme 25). The initial substrate represents an electron-deficient alkene bearing both an electron-withdrawing function (COOEt) and good leaving group (Cl). According to authors, the reaction proceeds through Michael addition and subsequent intramolecular substitution to afford three-membered ring derivative **29**. The preparation of compound **29** is chemoselective: no competing reactions such as direct S_N2 process or dehydrochlorination were observed in this case. The developed strategy could be successfully applied to the synthesis of a variety of functionalized small rings.



Scheme 25. Michael addition-induced synthesis of phosphonate cyclopropane ester.

Finally, unexpected and impressive reaction of captodative formyl(amino)alkenes with dialkyl phosphonates was discovered.[54,55] In fact, the treatment of unsaturated system **30** with H-phophonates under classical Pudovik reaction conditions did not lead to the expected 1,2- or 1,4-adducts. Instead, a cascade of transformations occurred to give the tertiary α-amino acids derivatives **31** (Scheme 26).

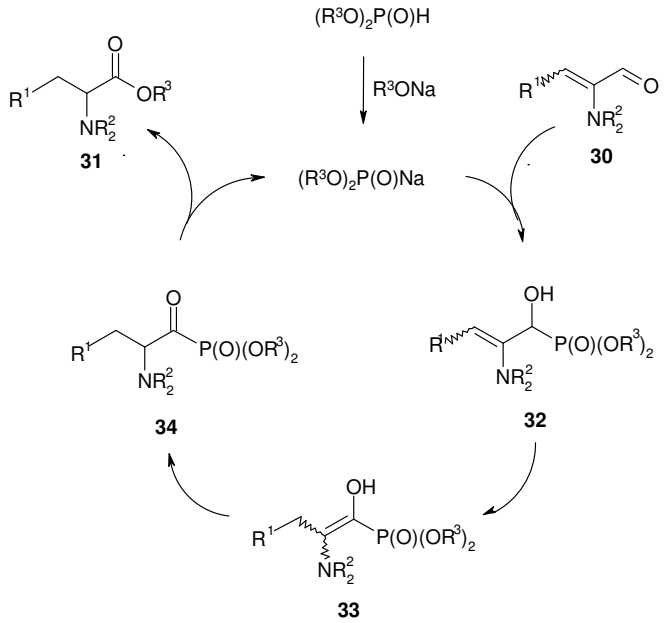
Evidently, the obtained results can be interpreted in terms of domino-reaction. The quite probable reaction pathway is depicted in Scheme 27.



Scheme 26. Unusual reaction of dialkyl phosphonates with captodative formyl(amino)alkenes.

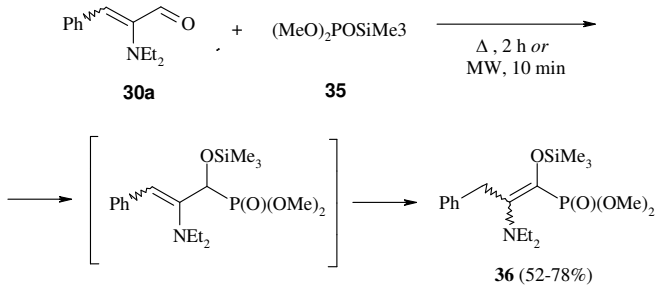
The key steps in the postulated mechanism are: nucleophilic attack on the carbonyl carbon of initial substrate to give 1,2-adduct **32**, which is able to undergo further cascade reactions involving the isomerization to more stable enol **33** which is further transformed into keto derivative **34**. The carbon-phosphorus bond in such derivatives is well known to be able to undergo a very easy cleavage under the action of nucleophiles (alcohol, amines etc) In a similar manner the ketophosphonate

34 under the action of alkoxide of sodium in alcohol affords the final α-aminoester **31** (Scheme 27).



Scheme 27. Postulated mechanism of vicarious assistance of dialkyl phosphonates.

To support this hypothesis the initial substrate was treated with dimethyl(trimethylsilyl)phosphite **35** under microwave activation and silyl enol ether **36** was isolated (Scheme 28). Moreover, when captodative formyl(amino)alkene **30a** reacted with dipropyl phosphonate under the action of MeONa in MeOH, the corresponding methyl ester was formed as a major reaction product. The results indicate that the dialkyl phosphonates provide a vicarious assistance to the alcohol addition and the construction of -CH(NR_2)COOR' moiety.



Scheme 28. Synthesis of silyl enol ether **36** as proof of the reaction mechanism.

Conclusions

The important contribution in the field of phospha-Michael reactions was carried out within the last few years. The significant progress was achieved in the development of new catalytic systems as well as regio- and stereoselective addition of H-phosphonates to activated alkenes. Recent advances in phospha-Michael reaction make it as a really powerful green and waste-free tool for generation of C-P bond. However, there are some problems that need to be solved in the near future. Among them, the addition of hydrogen phosphonates to electron-poor alkenes bearing either weakly polar or highly substituted double bond. The synthesis of chiral functionalized phosphonates by phospha-Michael reaction will remain the significant focus of chemical community. Finally, one of the most actual current trend in this field is an improvement of the waste/product ratio and development of new environmentally compatible processes.

Taking into account that this reaction is used particularly for the synthesis of bioactive molecules and analogues of natural compounds, it can be expected further remarkable findings in this field of organic chemistry.

Notes and references

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