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HETEROPOLY ACIDS: GREEN CHEMICAL CATALYSTS IN ORGANIC SYNTHESIS

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Abstract – Heteropoly acids have been used in various fields of organic synthesis mainly due to their characteristic features: they are cost-effective reagents that are strongly acidic, environmentally friendly, and highly efficient. This review addresses the significant advances in organic synthesis using heteropoly acids or their salts mainly from papers published in this century. These include (1) Friedel-Crafts reactions, (2) Prins reactions, (3) Mannich reactions, (4) Biginelli reactions, (5) other types of condensation, (6) protection and deprotection, and (7) miscellaneous reactions such as epoxide ring-opening reactions.

INTRODUCTION

Heteropoly acids (HPAs) are composed of oxygen linkages between hetero-atoms such as P and Si, and addenda atoms such as Mo and W. HPAs have various structures depending on the properties of their hetero-atoms. In general, HPAs can be classified into Keggin and Dawson structures, as shown in Figure 1.[1] One of the characteristic features of HPAs is their strong acidity: they are normally stronger than conventional Lewis acids and mineral acids such as $AlCl_3$, H_2SO_4 and HCl. The acid strength of HPAs in water decreases in the series: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$. Furthermore, HPAs can be multi-stepwise reduced by multi-electrons. One-electron transfer occurs at each step in neutral media and two-electron transfer in acidic media.

Based on these characteristics of HPAs, they have been used extensively in various fields of organic synthesis, including industrial applications.[2, 3] However, due to the numerous papers that have been presented on HPA-catalyzed oxidation and epoxidation, only selected reviews are shown for convenience.[4] In this review we focus on recent advances in acid-catalyzed transformations using HPAs

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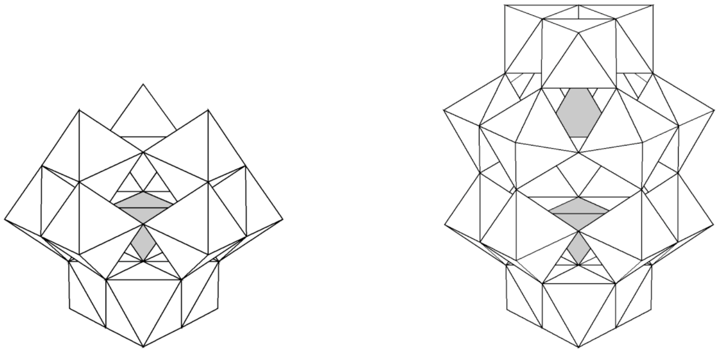
This paper is dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.



(a) (b)

Figure 1. The structures of HPAs: Keggin (a) and Dawson (b)

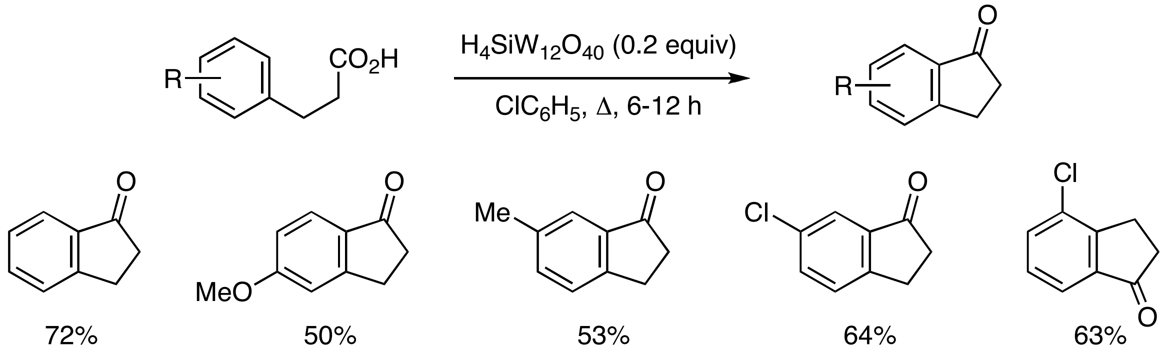
or their salts, with particular emphasis on papers published in this century.

An advantage of HPAs in organic synthesis is that they can be used in both homogeneous and heterogeneous reaction media. In addition, HPAs show many attractive features for synthetic chemists, such as flexibility in the design of their acid strength, recoverability, reusability, cost-effectiveness, non-corrosiveness, environment-friendliness, ease of handling, and experimental simplicity. In view of the increasing demand for the design of new green chemical processes in organic synthesis, HPA-catalyzed reactions offer an enormous field of synthetic challenges.

1. FRIEDEL-CRAFTS REACTIONS

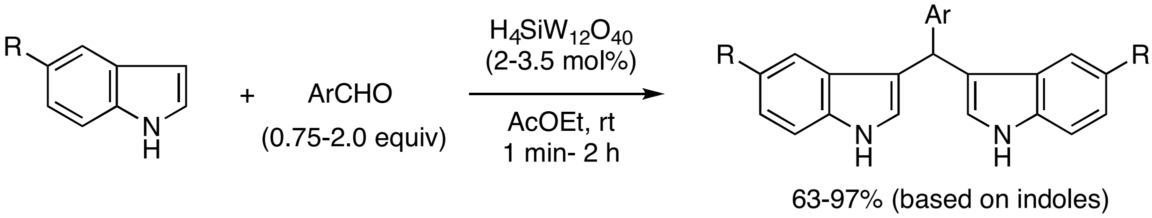
The strongly acidic nature of HPAs has provided a wide range of methods for Friedel-Crafts acylations and alkylations ever since organic chemists noticed their economical and environment-friendly characteristics.[5] Thus, several papers have been published from the viewpoint of synthetic interest, and also from industrial and mechanistic perspectives. Since the purpose of this review is to explore the synthetic value of HPAs in organic transformations, only representative examples will be shown.

The intramolecular Friedel-Crafts acylation of aryl acids can be achieved using HPAs as catalysts to give aromatic cycloketones such as 1-indanones (Scheme 1).[6,7]



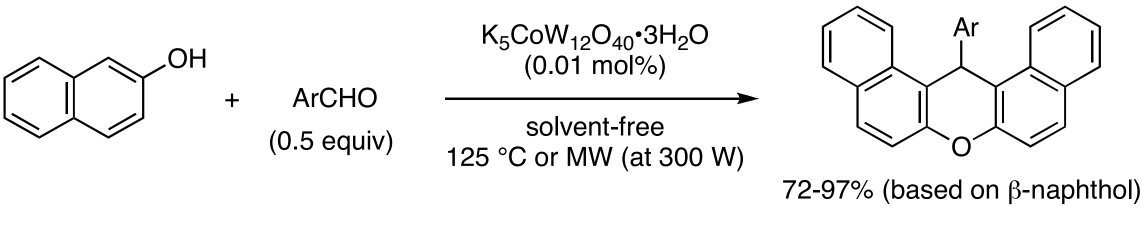
Scheme 1. HPA-catalyzed intramolecular Friedel-Crafts acylation

The electrophilic substitution of indoles with aromatic aldehydes produces the corresponding bis(indolyl)methane derivatives. Reactions of this type can be catalyzed efficiently by various kinds of HPAs under fairly mild conditions.[8-13] For example, when indoles were treated with aromatic aldehydes in the presence of a catalytic amount of $H_4SiW_{12}O_{40}$ in ethyl acetate at rt, the reactions were completed within 2 h to give the expected compounds in high yields (Scheme 2).[9] In an analogous situation, it has been shown that the alkylation of indoles with benzylic alcohols can be catalyzed by $H_3PMo_{12}O_{40}$ supported on silica gel with high yields and high selectivity.[14]



Scheme 2. HPA-catalyzed condensation of indoles with aromatic aldehydes

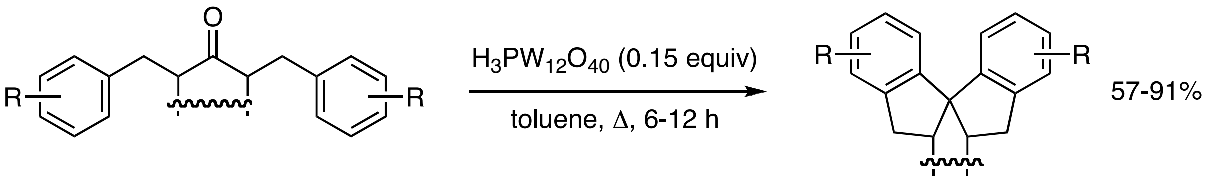
Instead of indoles, phenols can be used as donor molecules to efficiently prepare calix[4]arenes[15] and dibenzo[*a,j*]xanthenes.[16-18] For example, treatment of aromatic aldehydes with 2 equiv of β-naphthol in the presence of a catalytic amount of $K_5CoW_{12}O_{40}$ under solvent-free conditions using conventional heating (125 °C) or microwave irradiation (300 W) gave the expected products in high yields (Scheme 3).[18] It has also been shown that amidoalkyl naphthol synthesis can be achieved by a one-pot three-component coupling reaction of β-naphthol, aromatic aldehydes, and amides (or urea) in the presence of a catalytic amount of $K_5CoW_{12}O_{40}$ under solvent-free conditions.[19]



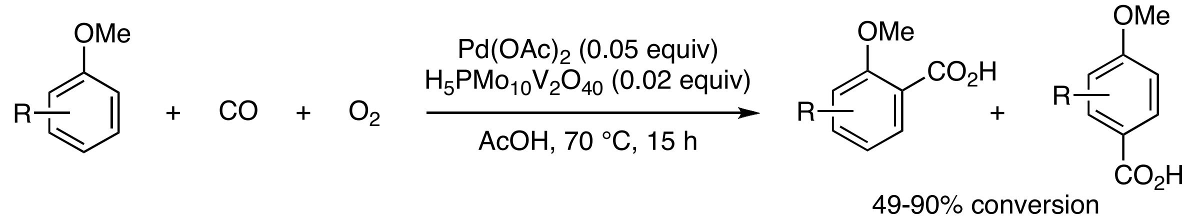
Scheme 3. HPA-catalyzed condensation of β-naphthol with aromatic aldehydes

The formation of 1,1'-spirobiindanes via bis-cyclization of 1,5-diaryl-3-pentanones occurs quite smoothly with $H_3PW_{12}O_{40}$ as a catalyst in refluxing toluene (Scheme 4).[20]

For other examples of aromatic functionalization, it has been reported that the cyclization of 1-phenyl-2-propen-1-ones into 1-indanones,[21] carboxylation of anisoles (Scheme 5),[22] the dimerization of styrenes or stilbenes,[23, 24] and indole- or pyrrole-alkylation with activated olefins[25] can be efficiently catalyzed by HPAs.

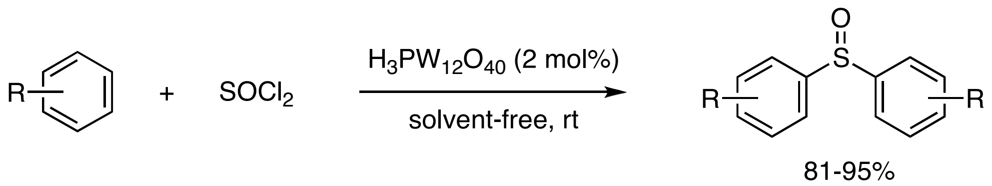


Scheme 4. HPA-catalyzed bis-cyclization of 1,5-diaryl-3-pentanones



Scheme 5. $Pd(OAc)_2$/HPA-catalyzed carboxylation of anisoles

The reaction of sufficiently reactive arenes with thionyl chloride in the presence of a catalytic amount of $H_3PW_{12}O_{40}$ provides an expeditious method for synthesizing diaryl sulfoxides (Scheme 6).[26]



Scheme 6. HPA-catalyzed synthesis of symmetrical diaryl sulfoxides

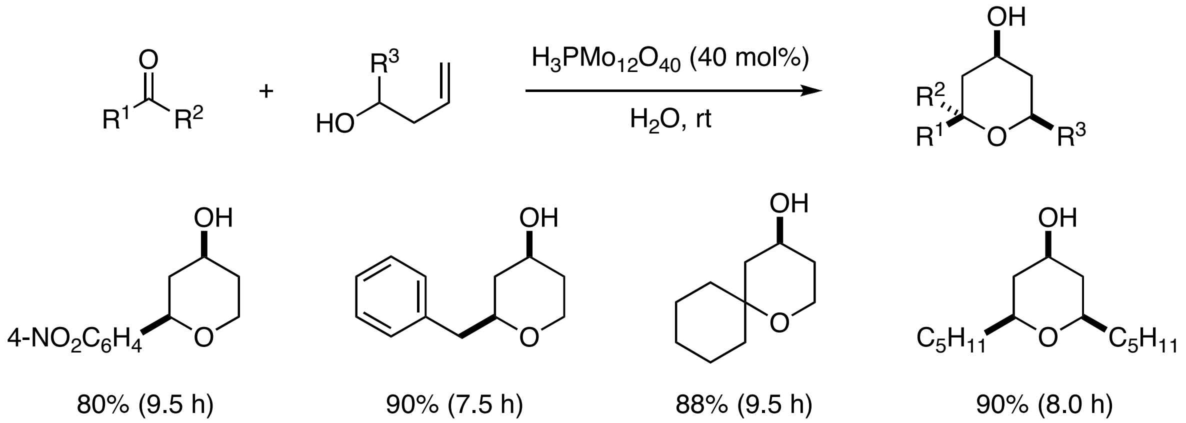
Finally, HPAs have been reported to be useful as catalysts for the Fries rearrangement of aryl esters.[27]

2. PRINS, MANNICH, AND BIGINELLI REACTIONS

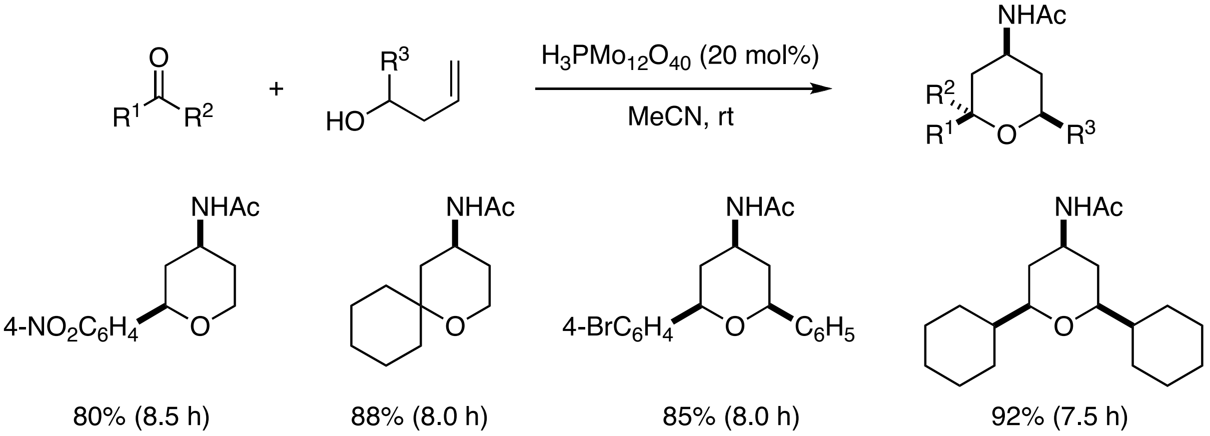
The acid-catalyzed condensation of olefins with aldehydes is known as the Prins reaction, and is conveniently used for the direct synthesis of tetrahydropyran derivatives. Recently, it has been shown that the use of HPAs is highly favorable, and such reactions can be facilitated even in water in the presence of $H_3PMo_{12}O_{40}$ as a catalyst, which gives an environmentally friendly process (Scheme 7).[28, 29]

Further extension of this methodology to the one-pot synthesis of 4-amidotetrahydropyran derivatives via the Prins-Ritter sequence has been reported (Scheme 8).[30] In these examples the desired products can be prepared in high yields exclusively with *cis*-selectivity.

The Mannich reaction is of great value for the direct synthesis of β-amino carbonyl compounds via the three-component condensation of amines, aldehydes and ketones. The reaction of this type is generally carried out in the presence of acid catalysts. In continuous efforts to develop environmentally friendly

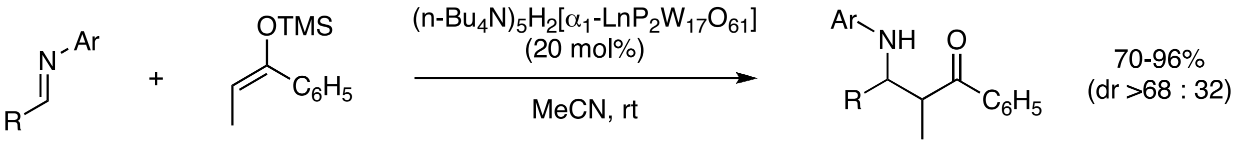


Scheme 7. HPA-catalyzed Prins cyclization



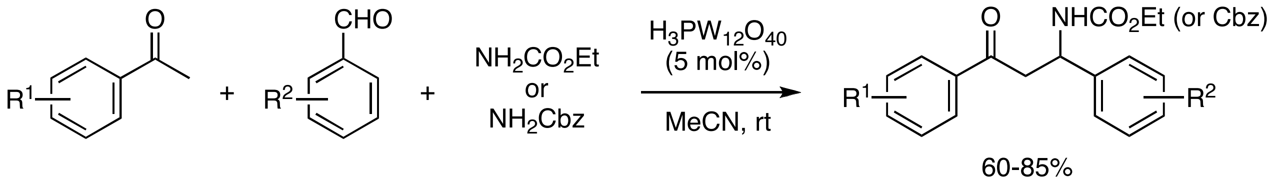
Scheme 8. HPA-catalyzed Prins-Ritter reaction

processes, HPA complexes containing a lanthanide metal have been shown to be useful as a new class of catalytic systems for the condensation of silyl enol ethers with imines (Scheme 9).[31, 32] The advantage of this method is the recoverability and reusability of the HPAs.



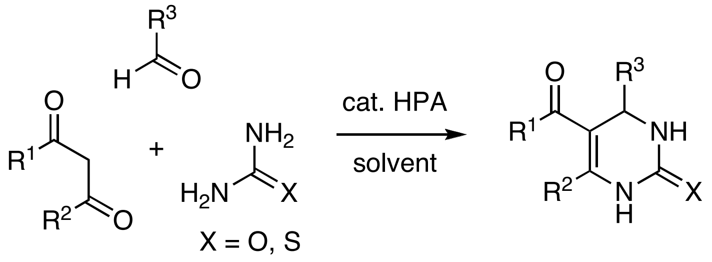
Scheme 9. Mannich-type condensation catalyzed by functionalized HPAs

Furthermore, in attempts to create new environmentally friendly systems, HPA-catalyzed Mannich reactions in water or in ionic liquid have recently been developed.[33, 34] Although there have been no precedents on the use of carbamates as amine components, it has been shown that the reactions can proceed smoothly by treatment with HPAs in MeCN at rt (Scheme 10).[35]



Scheme 10. HPA-catalyzed three-component Mannich reaction

The three-component condensation of aldehydes, β-keto esters, and urea, the so-called Biginelli reaction, provides a convenient way to produce pharmacologically important 3,4-dihydropyrimidinone derivatives. A reaction of this type is generally performed with strong protic or Lewis acid catalysts. However, due to the increasing desire for environmentally friendly processes, much attention has recently been focused on the use of HPAs and their salts. In fact, a variety of reagents have been developed, such as $Ag_3PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $K_5CoW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4PMo_{11}VO_{40}$, and $H_6P_2W_{18}O_{62}$ (Scheme 11).[36-49] Interestingly, HPAs with no acidic protons such as $Ag_3PW_{12}O_{40}$ and $K_5CoW_{12}O_{40}$, still possess sufficient catalytic activity.[36, 46]



HPA:
$Ag_3PW_{12}O_{40}$ (Ref 36; H_2O or EtOH, <96%)
$H_3PW_{12}O_{40}$ (Ref 37; EtOH or MeCN, <94%)
$H_3PMo_{12}O_{40}$ (Ref 45; AcOH, <80%)
$K_5CoW_{12}O_{40}$ (Ref 46; solvent-free, <95%)
$H_4SiW_{12}O_{40}$ (Ref 47; AcOH, <91%)
$H_4PMo_{11}VO_{40}$ (Ref 48; EtOH, <96%)
$H_6P_2W_{18}O_{62}\cdot 24H_2O$ (Ref 49; solvent-free, <99%)

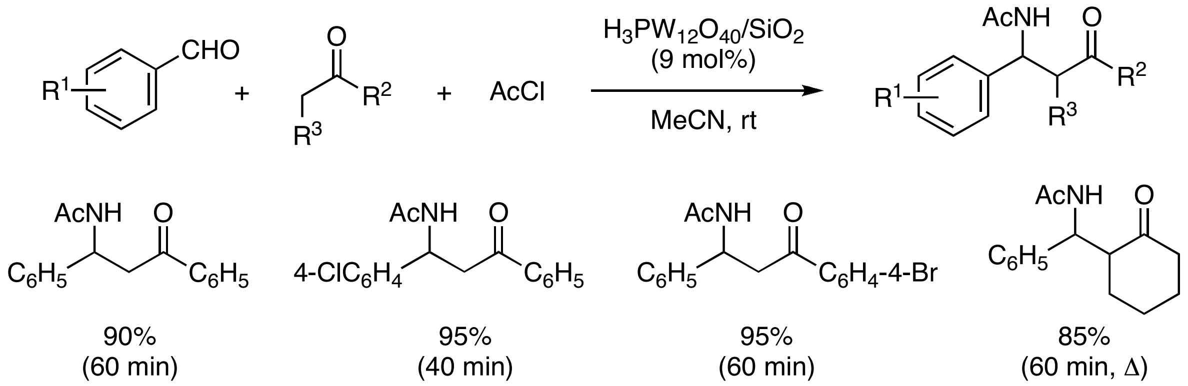
Scheme 11. HPA-catalyzed Biginelli reaction

3. OTHER TYPES OF CONDENSATION

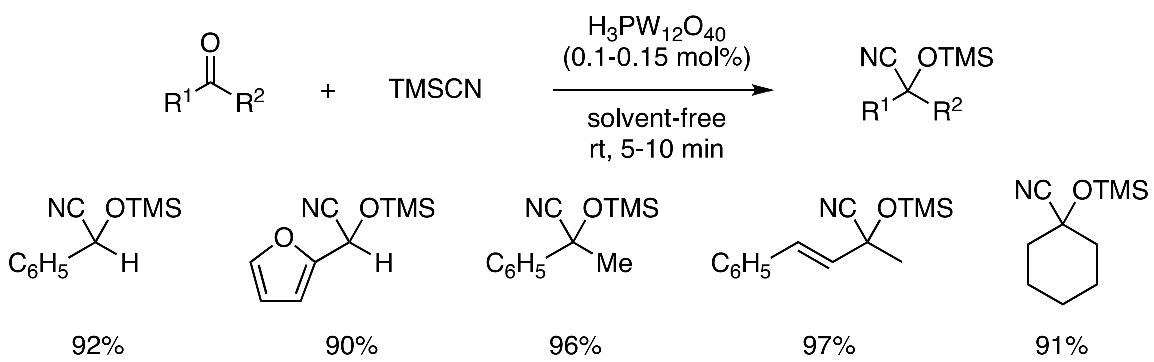
The environmentally friendly and strongly acidic character of HPAs has been applied to other types of condensation reactions. The Dakin-West reaction, a convenient way to produce β-acetamido ketone derivatives via four-component coupling of aryl aldehydes, ketones, acetyl chloride and acetonitrile, can be efficiently catalyzed by HPAs (Scheme 12).[50-54]

Cyanohydrin synthesis by the action of TMSCN upon carbonyl compounds can also be facilitated by a catalytic amount of $H_3PW_{12}O_{40}$ under solvent-free conditions (Scheme 13).[55] In a similar manner, the Strecker reaction for the synthesis of α-amino nitriles can be performed in the presence of $H_{14}[NaP_5W_{30}O_{110}]$ or $H_3PW_{12}O_{40}$ supported on silica gel as a catalyst.[56, 57]

Due to their pharmaceutical and industrial importance, there are thousands of methods available for the synthesis of heterocycles, and this is why many famous named reactions have been introduced. The Friedeländer quinoline synthesis is a typical example, which can be performed by the acid-catalyzed

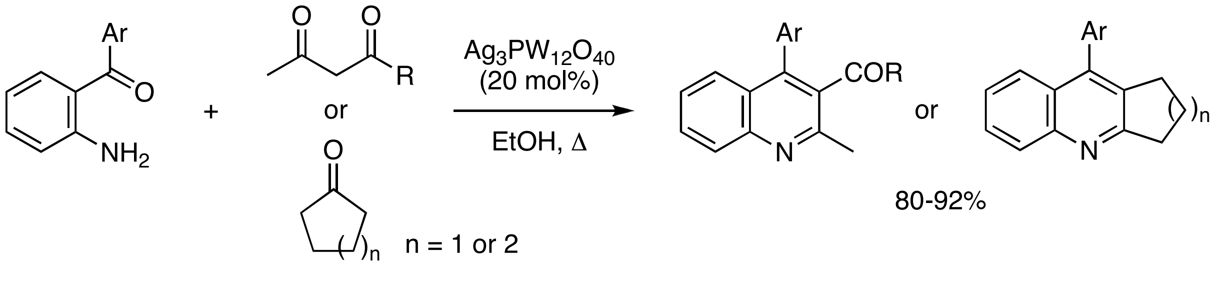


Scheme 12. HPA-catalyzed Dakin-West reaction



Scheme 13. HPA-catalyzed synthesis of cyanohydrin TMS-ethers

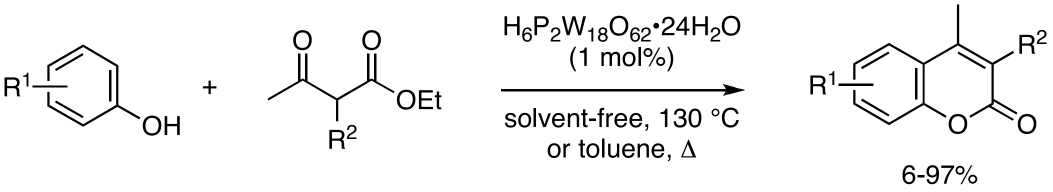
condensation of anilines with ketone substrates. In this area, HPAs again play an important role in environmentally friendly acid-catalyzed systems (Scheme 14).[58]



Scheme 14. HPA-catalyzed Friedländer quinoline synthesis

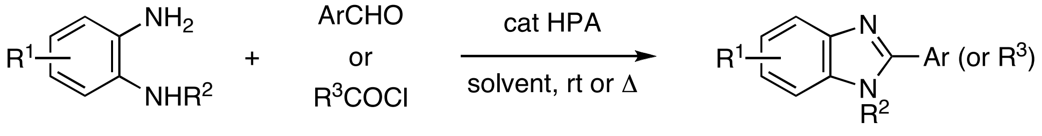
The use of $H_4SiW_{12}O_{40}$ or $K_5CoW_{12}O_{40}$ in Skraup synthesis[59, 60] and $H_3PW_{12}O_{40}$ in Doebner-Miller synthesis[61] has been reported.

Coumarins and related compounds can be prepared by the acid-catalyzed condensation of phenols with β-ketoesters, and various types of HPAs have been used for this purpose. For example, it has been shown that $H_6P_2W_{18}O_{62}$ is useful for the synthesis of a variety of 4-substituted coumarin derivatives in refluxing toluene or under solvent-free conditions (Scheme 15).[62] Other types of catalysts are also effective for related reactions.[63, 64] In addition, the HPA-catalyzed synthesis of chromones and chromenes,[65-68] and quinolones[69, 70] has been reported.



Scheme 15. HPA-catalyzed synthesis of 4-substituted coumarins

The acid-catalyzed condensation of *o*-phenylenediamines with aldehydes or acyl chlorides can serve as an efficient entry to prepare benzimidazole derivatives, and HPAs have again been shown to be useful in this area (Scheme 16).[71-74] Tetrasubstituted imidazole derivatives can be prepared conveniently by the four-component condensation of 1,2-diketones, aldehydes, amines and ammonium acetate.[75, 76] Instead, the condensation of 1,2-diketones with *o*-phenylenediamines gives quinoxaline derivatives.[77] The superiority of HPAs in these reactions over conventional catalysts is apparent from their recoverability, reusability, experimental simplicity and high yields.



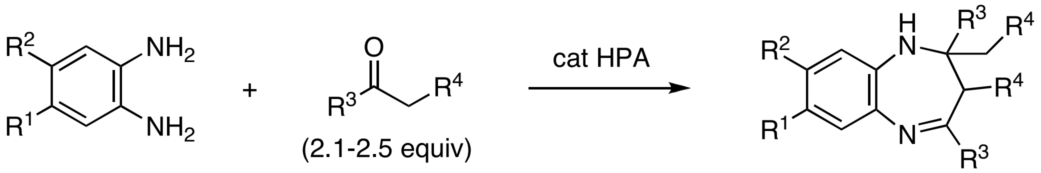
HPA: $H_4SiW_{12}O_{40}$ (Ref 71; AcOEt, rt, 52-99%)
$(NH_4)H_2PW_{12}O_{40}$ (Ref 72; $ClCH_2CH_2Cl$, Δ, 84-94%)
$H_5PMo_{10}V_2O_{40}$ (Ref 73; MeCN, Δ, <99%)

Scheme 16. HPA-catalyzed synthesis of benzimidazoles

The three-component condensation reaction of *o*-phenylenediamines with 2.0 equiv of ketones can proceed smoothly in the presence of HPAs as catalysts to afford the corresponding 1,5-benzodiazepine derivatives in high yields (Scheme 17).[78-82]

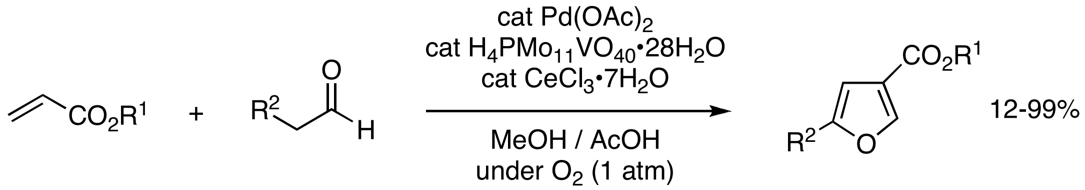
Several examples of the short-cut synthesis of 5-membered heterocycles under catalysis with HPAs have been reported. Typical examples include furans from acrylates and aldehydes (Scheme 18),[83] pyrroles from amines, aldehydes and nitroalkenes (Scheme 19),[84] isoxazoles from 1,3-diketones and hydroxyl amine,[85] and oxazolines, imidazolines and thiazolines from nitriles (Scheme 20).[86, 87]

For other types of HPA-catalyzed dehydrative condensations for the synthesis of heterocycles[88-91] and for the Knoevenagel condensation,[92] only references are shown for convenience.

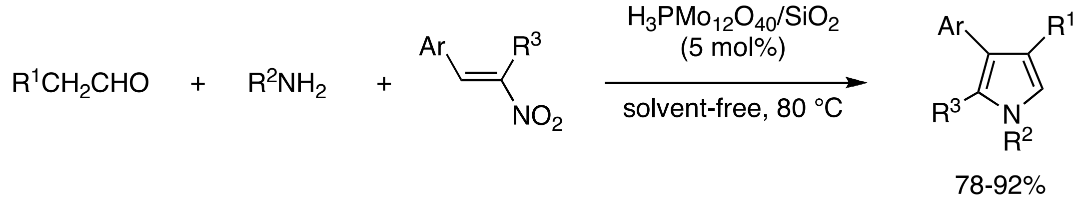


HPA	conditions	yield	Ref
$Ag_3PW_{12}O_{40}$ (30 mol%)	solvent-free, rt	72-95%	[78]
$(NH_4)H_2PW_{12}O_{40}$ (5 wt%)	$ClCH_2CH_2Cl$, Δ	88-95%	[79]
$H_{14}[NaP_5W_{30}O_{110}]$ (0.1 mol%)	EtOH, Δ	80-95%	[81]
$AlPW_{12}O_{40}$ or $AlPMo_{12}O_{40}$ (5 or 6 mol%)	solvent-free, rt	82-98%	[82]

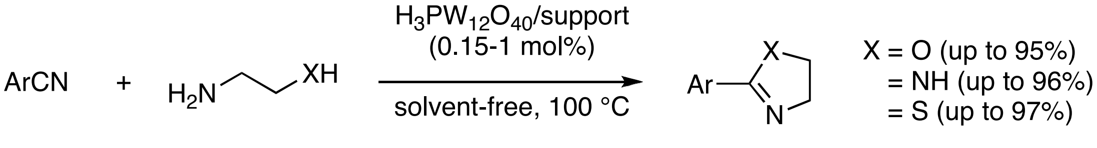
Scheme 17. HPA-catalyzed synthesis of 1,5-benzodiazepines



Scheme 18. $Pd(OAc)_2/HPA/CeCl_3/O_2$ promoted synthesis of furoates



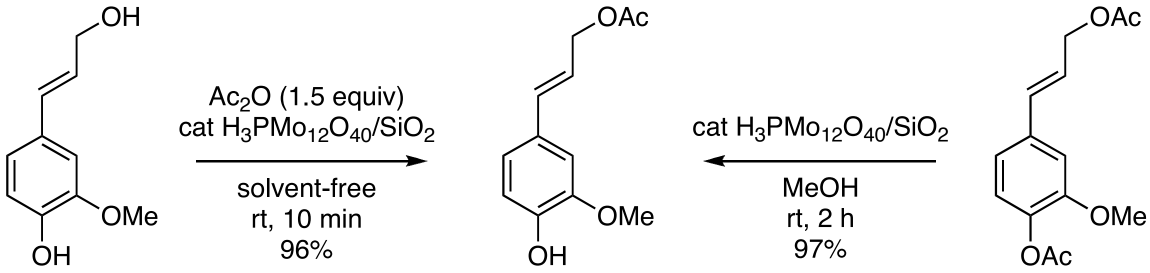
Scheme 19. HPA-catalyzed synthesis of substituted pyrroles



Scheme 20. HPA-catalyzed synthesis of oxazolines, imidazolines, and thiazolines

4. PROTECTION AND DEPROTECTION

Acylation of alcohols, phenols and amines is a fundamental technique in protective chemistry, and acid or base catalysts are generally used for this purpose. Catalytic systems based on HPAs offer several advantages due to their environmentally friendly character. Along this line, several examples of HPA-catalyzed acylation reactions have been reported.[93-100] For example, Das and coworkers have shown that $H_3PMo_{12}O_{40}$ supported on silica gel could serve as an efficient catalyst for the selective acetylation of alcohols, phenols and amines under solvent-free conditions, and also for the chemoselective deprotection of phenyl acetates under fairly mild conditions (Scheme 21).[98]



Scheme 21. HPA-catalyzed chemoselective acetylation and deacetylation

The protection or deprotection of somewhat sensitive functionalities with a Si group,[101-104] THP group,[105-107] MOM group,[108, 109] Ts group,[110] Boc group,[111] and others[112] has been performed efficiently in the presence of HPAs as catalysts (Scheme 22).

$$R{-}XH \quad + \quad \text{protective agent} \quad \xrightarrow[\text{conditions}]{\text{cat HPA}} \quad R{-}XP \qquad P = \text{protective group}$$

ROH → ROTMS [Ref 101]
$H_3PW_{12}O_{40}$ (1 mol%) / $(Me_3Si)_2NH$ (0.8 equiv)
conditions: solvent-free, 55-60 °C
yield up to 100%

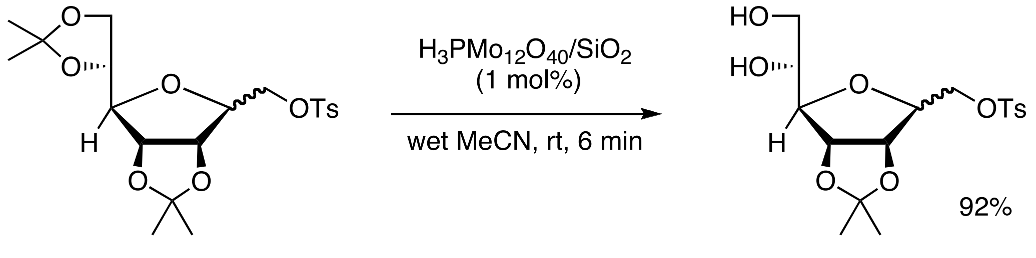
ROH → ROTs [Ref 110]
$AlPW_{12}O_{40}$ or $AlPMo_{12}O_{40}$ (3 mol%) /
TsCl (1.2 equiv)
conditions: solvent-free, rt
yield up to 100%

ROH → ROTHP [Ref 107]
$H_{14}[NaP_5W_{30}O_{110}]$ (0.1 mol%) / DHP (1.1 equiv)
conditions: CH_2Cl_2, Δ
yield up to 94%

RR'NH → RR'NBoc [Ref 111]
$H_3PW_{12}O_{40}$ (0.5 mol%) / Boc_2O (0.9 equiv)
conditions: CH_2Cl_2, rt
yield up to 98%

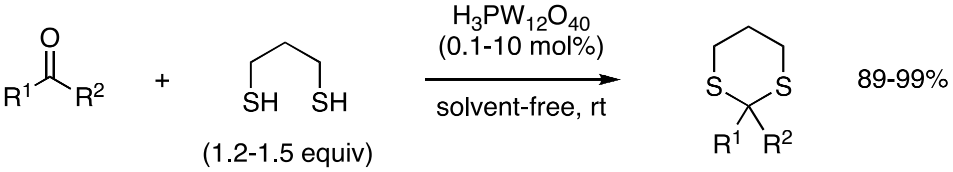
Scheme 22. HPA-catalyzed protection of alcohols and amines

Recently, the use of $H_3PMo_{12}O_{40}$ supported on silica gel was found to be highly effective for the chemoselective deprotection of acetonides, as exemplified in Scheme 23.[113] Interestingly, all reactions are completed within a very short period of time with excellent yields.



Scheme 23. HPA-catalyzed chemoselective deprotection of acetonides

The protection of carbonyl groups as their acetals or dithioacetals can be an essential tool in the organic synthesis of multi-functional compounds, and such reactions generally require the use of relatively strong acids. During the search for new efficient catalytic systems, it has been shown that HPAs or their salts are very effective as heterogeneous catalysts.[114-118] A typical example is shown in Scheme 24, where the catalytic activity of $H_3PW_{12}O_{40}$ is reported to be much higher than that of conventional acid catalysts such as H_2SO_4, $MeSO_3H$, and CF_3SO_3H.[114]



Scheme 24. HPA-catalyzed dithioacetalization of aldehydes or ketones

The protection of aldehydes as their 1,1-diacetate derivatives, i.e. acylals, can also be efficiently catalyzed by HPAs or their salts under solvent-free conditions (Scheme 25).[119-124]

$$\mathrm{RCHO} + \mathrm{Ac_2O} \xrightarrow[\text{neat}]{\text{cat HPA}} \mathrm{RCH(OAc)_2}$$

HPA:
$H_6P_2W_{18}O_{62}\cdot 24H_2O$ (Ref 119; 88-98%)
$AlPW_{12}O_{40}$ (Ref 120; 88-96%)
$H_3PMo_{12}O_{40}$ (Ref 121; 92-99%)
$H_6PAlMo_{11}O_{40}$ (Ref 124; 87-100%)

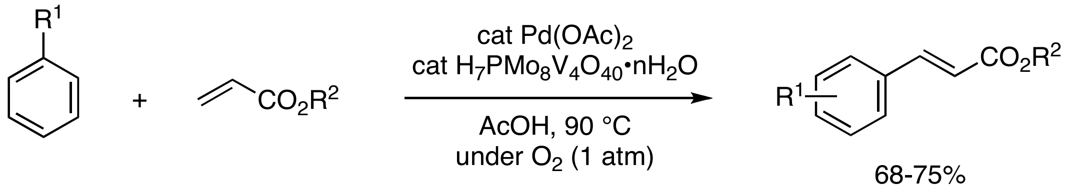
Scheme 25. HPA-catalyzed preparation of acylals from aldehydes

There have been several reports on the novel use of HPAs as catalysts for the oxidative deprotection of oximes to the parent carbonyl compounds[125-127] and the oxidative deamination of *N*-amino nitrogen heterocycles.[128]

5. MISCELLANEOUS REACTIONS

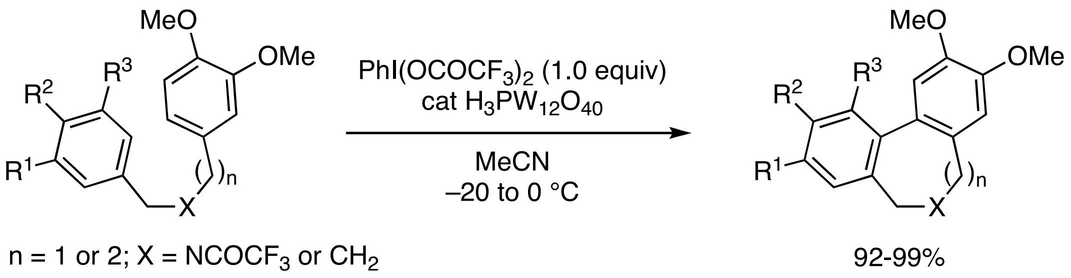
Aromatic nitro-compounds are of great industrial importance as a source of dyes, pharmaceuticals, perfumes, and plastics. Thus, various methods have been reported to prepare these compounds. The most popular is the use of nitric and sulfuric acids. However, this has several drawbacks, such as corrosiveness and a potential danger of explosion. Recently, it has been shown that HPAs such as $H_5PMo_{10}V_2O_{40}$ can be conveniently used for the nitration of aromatic compounds under environmentally friendly conditions.[129, 130] A reagent of this type is also effective for the nitration of alkanes.[131] In some cases, HPAs can also act as efficient catalysts for aromatic bromination and iodination.[132-134]

On the other hand, the Heck-Mizoroki-type coupling of benzenes with acrylates can be achieved efficiently by the use of a catalytic amount of $Pd(OAc)_2$ combined with $H_7PMo_8V_4O_{40}$ under oxygen (Scheme 26).[135] A related reagent system has also been found to be effective for the dimerization of benzenes.[136]



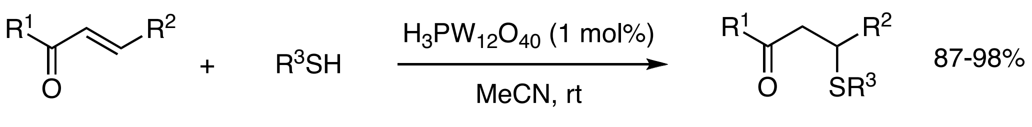
Scheme 26. $Pd(OAc)_2$/HPA catalyzed Heck-Mizoroki-type arylation

The combination of HPAs with hypervalent iodine(III) reagent is an efficient protocol for the synthesis of a variety of biaryl compounds via the intramolecular oxidative coupling of phenyl ether derivatives (Scheme 27).[137, 138]



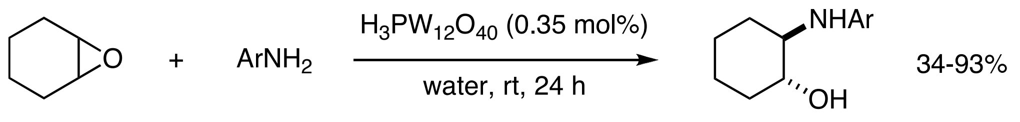
Scheme 27. HPA-catalyzed oxidative coupling of phenyl ethers

The conjugate addition of thiols to α,β-unsaturated ketones can be catalyzed by $H_3PW_{12}O_{40}$ (1 mol%) in MeCN to give the corresponding Michael adducts within 60 min at rt (Scheme 28).[139]



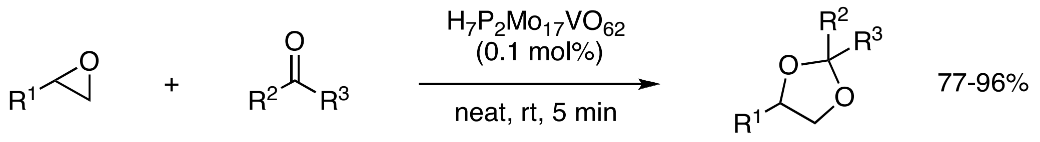
Scheme 28. HPA-catalyzed conjugate addition of thiols to enones

The aminolysis of epoxides is an important tool for the synthesis of pharmacologically interesting β-amino alcohol derivatives. Towards this end, HPAs can be conveniently used as highly effective, commercially available, and environmentally friendly catalysts.[140-143] For example, when cyclohexene oxide was treated with 1.0 equiv of anilines in the presence of $H_3PW_{12}O_{40}$ (0.35 mol%) in water at rt, the corresponding amino alcohol derivatives were obtained in good yields (Scheme 29).[144]



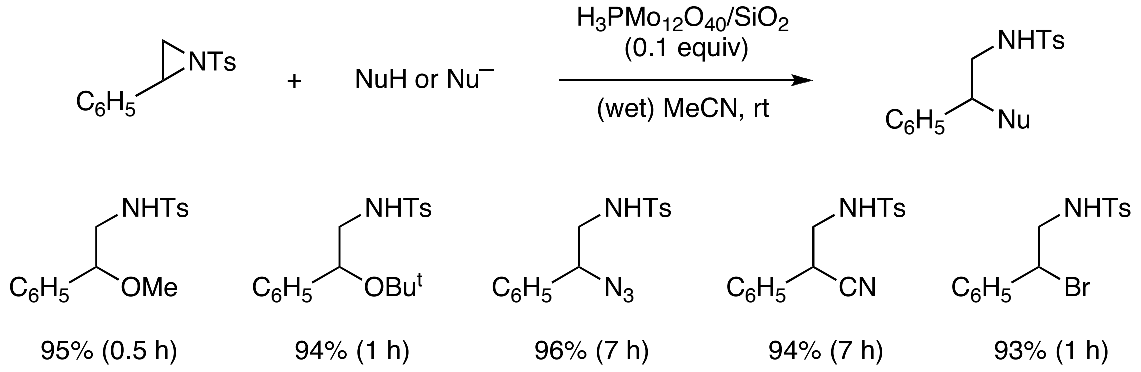
Scheme 29. HPA-catalyzed epoxide ring-opening reaction with anilines

On the other hand, HPA-catalyzed reactions of epoxides with ketones provide an efficient entry to 1,3-dioxolane derivatives (Scheme 30).[145, 146]



Scheme 30. HPA-catalyzed conversion of epoxides to 1,3-dioxolanes

Furthermore, the ring-opening reactions of aziridines with a variety of nucleophiles can be effectively catalyzed by $H_3PMo_{12}O_{40}$ supported on silica gel (Scheme 31).[147]

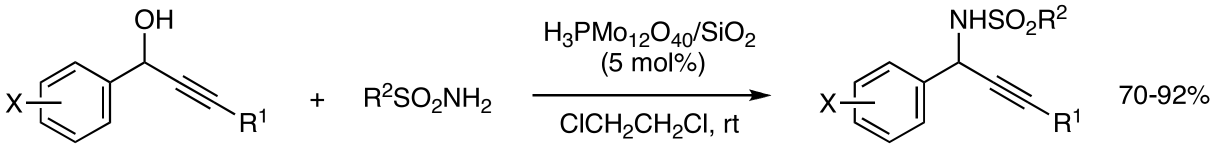


Scheme 31. HPA-catalyzed ring-opening reaction of aziridines

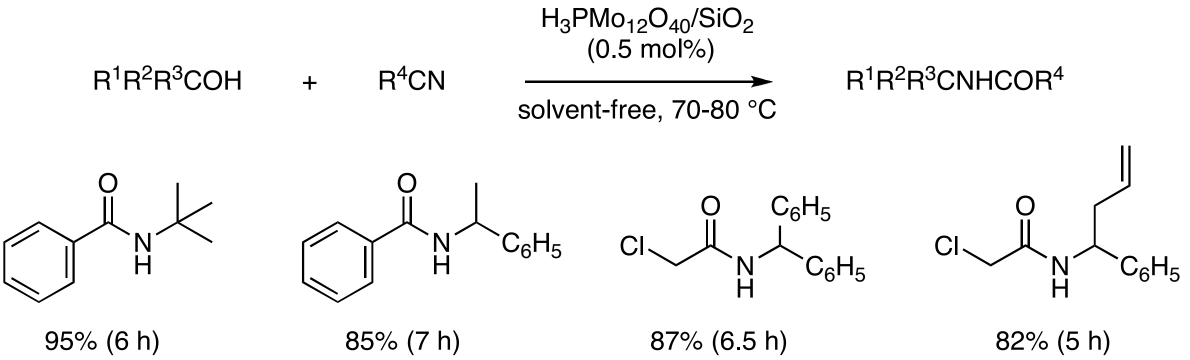
In some cases, HPA can act as a novel nitrene transfer agent in the production of aziridines from olefins in the presence of Chloramine-T.[148]

Various methods have been reported for the direct substitution of moderately reactive secondary and tertiary alcohols with *O*- or *N*-nucleophiles in the presence of a catalytic amount of HPA (Scheme 32).[149-151] An important application in this area is the Ritter reaction: the amidation of alcohols in the presence of nitriles proceeds cleanly under catalysis with $H_3PMo_{12}O_{40}$ supported on silica gel (Scheme 33).[152]

In some cases, HPAs can act as efficient catalysts to promote a cross-coupling reaction between aryl/alkyl halides and thiols to produce the corresponding thioethers under fairly mild conditions.[153]

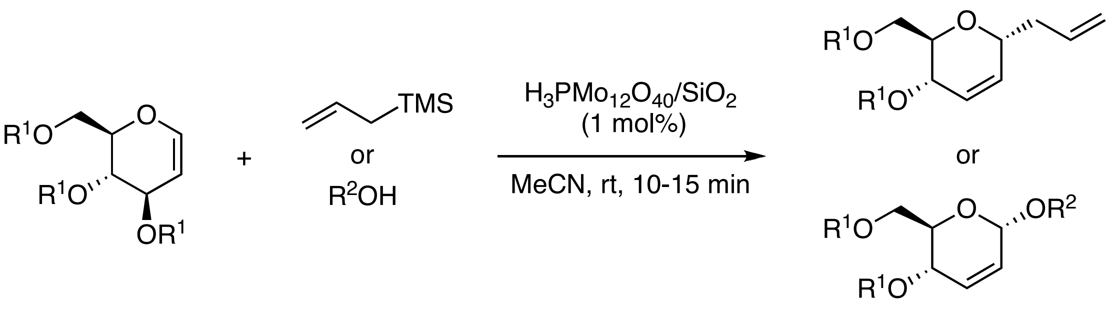


Scheme 32. HPA-catalyzed substitution of 2-propynyl alcohols



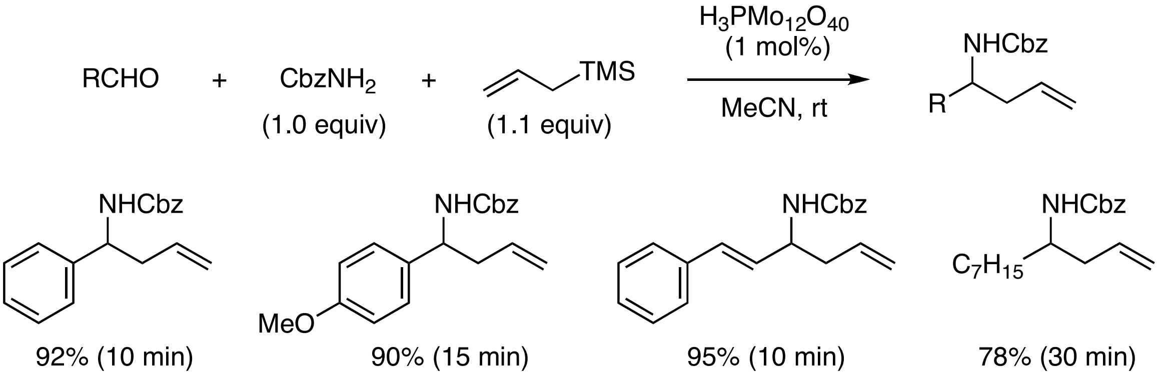
Scheme 33. HPA-catalyzed Ritter reaction of alcohols with nitriles

The acid-catalyzed allylic rearrangement of glycals in the presence of appropriate nucleophiles is known as the Ferrier rearrangement. A reaction of this type can also be efficiently catalyzed by $H_3PMo_{12}O_{40}$ supported on silica gel: in the presence of allyltrimethylsilane or alcohols as nucleophiles the corresponding 2,3-unsaturated allyl *C*- or *O*-glycosides can be obtained in high yields with excellent α-selectivity (Scheme 34).[154]



Scheme 34. HPA-catalyzed Ferrier rearrangement of glycals

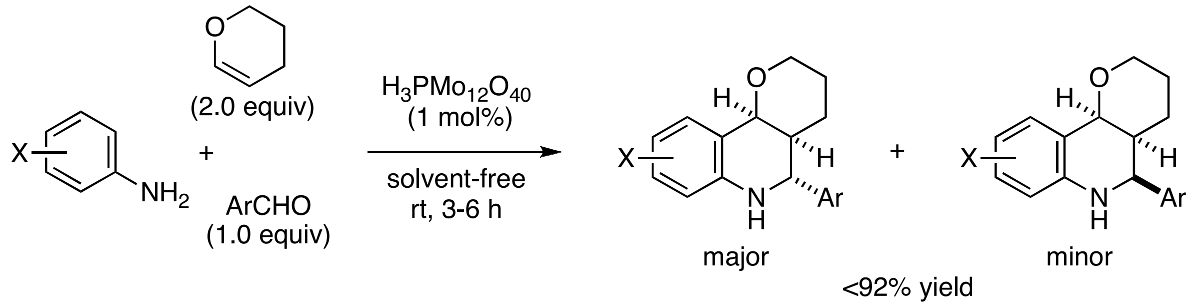
The high catalytic activity of HPAs has been further demonstrated in a successful three-component coupling reaction of aldehydes, carbamates, and allyltrimethylsilane.[155, 156] For example, treatment of a mixture of aldehydes, benzyl carbamate ($CbzNH_2$) and allyltrimethylsilane with $H_3PMo_{12}O_{40}$ (1 mol%) in MeCN at rt provides the corresponding Cbz-protected homoallylic amines in good yields (Scheme 35).[155]



Scheme 35. HPA-catalyzed three-component coupling reaction

The synthetic utility of HPAs or their salts as catalysts in the hydroamination of alkynes has also been reported.[157-159] Recently, it has been shown that the combination of chiral amines with HPAs could serve as efficient and recoverable catalysts in organocatalytic asymmetric aldol reactions.[160]

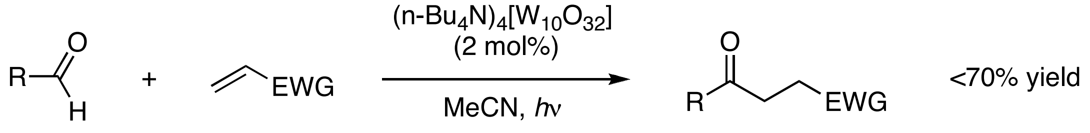
Some successful examples of the use of HPAs as acid catalysts in cycloaddition reactions including aza-Diels-Alder and 1,3-dipolar cycloadditions, have been reported.[31, 161-163] For example, the reaction of anilines, aldehydes and cyclic enol ethers in the presence of $H_3PMo_{12}O_{40}$ provides an efficient entry to *trans*-fused pyrano- and furanoquinoline derivatives via an aza-Diels-Alder reaction under solvent-free conditions (Scheme 36).[163]



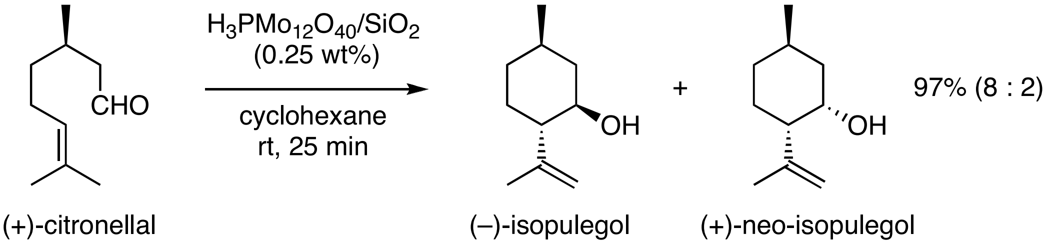
Scheme 36. HPA-catalyzed aza-Diels-Alder reaction

Albini and coworkers have investigated the feasibility of HPA salts in the photochemical alkylation of electrophilic olefins.[164-167] The photocatalytic synthesis of unsymmetrical ketones using aldehydes and electrophilic olefins as starting substrates is particularly interesting from the viewpoint of synthetic economy (Scheme 37).[167] In this sequence it is conceivable that the photoactivated HPA salts abstract the hydrogen atom from aldehydes, which leads to reasonably reactive acyl radicals which then combine with olefins to give the end products in good yields.

As shown in Scheme 38, ene-cyclization of (+)-citronellal to (–)-isopulegol proceeds smoothly upon exposure to $H_3PMo_{12}O_{40}$ supported on silica gel in cyclohexane at rt within a short period of time.[168, 169]

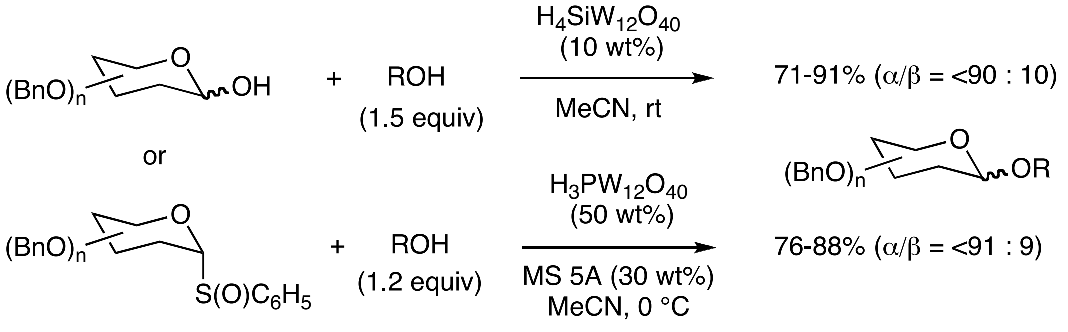


Scheme 37. Photocatalyzed acylation of activated olefins in the presence of HPA salts



Scheme 38. HPA-catalyzed cyclization of (+)-citronellal

Chemo- and stereoselective glycosidation is an extremely important issue in carbohydrate chemistry, and hence several reagents and catalysts have been developed to date. Although the use of HPAs in this area seems to be limited, in some cases chemo- and stereoselective glycosidation can be achieved, e.g., starting from hydroxy or sulfinyl sugars (Scheme 39).[170, 171] As a closely related system, the α-selective glycosidation of tri-*O*-acetyl-D-glucal with alcohols has been reported.[172]



Scheme 39. HPA-catalyzed α-selective glycosidation

Due to the increasing importance of bio-fuel production, technological improvements for the degradation of agricultural raw materials are of great interest. Recently, it has been shown that HPAs and their salts might be useful for this purpose.[173-175] The dehydration of alcohols as well as dehydrative cyclization can be catalyzed by HPAs supported on silica gel.[176]

The intermolecular hydroamination of vinyl arenes[177] and chemoselective oximation of aldehydes[178] are both effectively catalyzed by HPAs under solvent-free conditions. HPAs have also been shown to be useful for a variety of functional group transformations such as the reductive amination of aldehydes or ketones,[179] 1,2-reduction of α,β-unsaturated aldehydes or ketones,[179] and aromatization of

1,2-dihydroquinolines.[180]

CONCLUSION

Based on the findings described above, HPAs are clearly superior to conventional acid catalysts such as $AlCl_3$, H_2SO_4 and CF_3SO_3H, since HPAs are easy to handle, non-corrosive, economical, and environmentally friendly. In many cases the reactions can be achieved under fairly mild conditions using solvent-free and aqueous media, and can be completed within a short period of time with excellent chemoselectivity. In addition, HPAs are conveniently recoverable and reusable without a considerable loss of activity. In view of the keen demand for new green and eco-friendly processes, further effort should be made to explore truly valuable synthetic applications. We hope that dramatic progress will be made in the near future.

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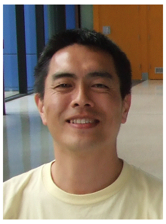

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