# Diels–Alder reactions of carbonyl-containing dienophiles catalyzed by tungstophosphoric acid supported on silica gel

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Tungstophosphoric acid ($H_3PW_{12}O_{40}$) supported on silica gel proved to be an active heterogeneous catalyst for Diels–Alder reactions of enones with various dienes. The Diels–Alder adducts were formed in high regio- and/or stereoselectivity. In some cases the Diels–Alder reactions were accompanied by competing polymerization of the starting compounds. We also found that trifluoromethanesulfonic acid (triflic acid) is an effective homogeneous catalyst for the reaction of unprotected but-3-en-2-one (methyl vinyl ketone) with 1,3-cyclohexadiene, albeit with a lower activity than tungstophosphoric acid.

**Keywords:** heteropoly acids, Diels–Alder reaction, heterogeneous catalyst, triflic acid

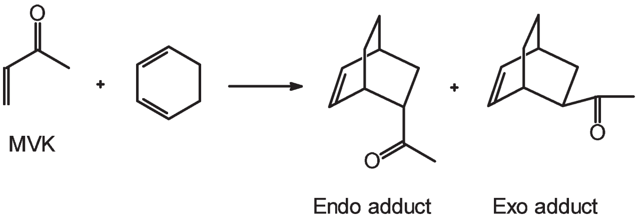
## 1. Introduction

Heteropoly acids (HPAs) have found widespread application as catalysts for organic reactions [1–3]. Especially the HPAs belonging to the so-called Keggin series are employed as both acid catalysts and oxidation catalysts. Examples of the former include aromatic alkylations, esterifications, isomerizations, and polymerizations and examples of the latter include the oxidation of, e.g., alkanes, alkenes, and alcohols. Recently, we showed that tungstophosphoric acid ($H_3PW_{12}O_{40}$) supported on silica gel is an active heterogeneous catalyst for Diels–Alder reactions of quinones [4]. This catalyst extends the series of known heterogeneous catalysts for Diels–Alder reactions such as Nafion-H [5], clays [6–9], zeolites [10–14], silica [15], alumina [16], and an aluminium silasesquioxane gel [17]. The use of such solid acids facilitates the recovery and recycling of the catalyst. Here we report on the extension of the scope of our discovery to Diels–Alder reactions of unsaturated aldehydes and ketones.

## 2. Results and discussion

Initially, we investigated the Diels–Alder reaction of methyl vinyl ketone (MVK) with 1,3-cyclohexadiene (scheme 1). It has been reported previously that no reaction between these substrates was observed after 24 h at 25 °C [18]. In contrast, in the presence of a catalytic amount of 40 wt% $H_3PW_{12}O_{40}$ on silica gel (prepared by impregnation with an aqueous solution) the reaction proceeded smoothly at 0 °C in dichloromethane (see table 1). With ca. 0.5 mol% catalyst the Diels–Alder adduct was obtained in 93% isolated yield after 4 h, and in high *endo* selectivity (96%). A lower activity was observed with a regenerated catalyst (entry 2). This is probably due to poisoning of the catalyst surface by oligomeric and polymeric by-products formed during the reaction.

We also investigated the performance of soluble Brønsted acids in the reaction of MVK with 1,3-cyclohexadiene. Bulk HPAs dissolve readily in polar solvents, but initial experiments with tungstophosphoric acid, in ethanol, acetone or ethyl acetate, as homogeneous catalyst for Diels–Alder reactions showed lower activities and selectivities than the supported HPA. Trifluoromethanesulfonic acid (triflic acid) is comparable in acid strength to tungstophosphoric acid [19] and was previously reported [20] to catalyze the Diels–Alder reaction of the ethylene glycol acetal of MVK with 1,3-cyclohexadiene. The reaction was carried out in dichloromethane at low temperature (from −78 to 10 °C) with 2 mol% of triflic acid and gave the adduct in 78% yield. We have found that the unprotected ketone can also be used as substrate. With 0.1 mol% of triflic acid we observed 50% conversion of MVK after 6 h at 25 °C, i.e., a lower activity than that of $H_3PW_{12}O_{40}$ on silica gel (cf. table 1, entries 3 and 4). Under optimum conditions with triflic acid (1 mol% at 0–20 °C) the Diels–Alder adduct was isolated in 84% yield.



Scheme 1. The Diels–Alder reaction of methyl vinyl ketone and 1,3-cyclohexadiene.

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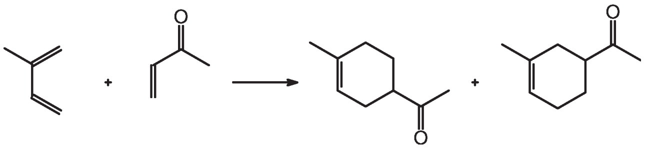
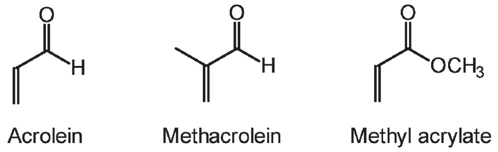
Table 1
Diels–Alder reactions of MVK catalyzed by $H_3PW_{12}O_{40}$ supported on silica gel.[a]

| Entry | Diene | Cat. (mol%) | $T$ (°C) | $t$ (h) | Yield[b] (%) | Selectivity[c] |
|---|---|---|---|---|---|---|
| 1 | 1,3-cyclohexadiene | 0.48 | 0 | 4 | 94[d] | 96/4[e] |
| 2 | 1,3-cyclohexadiene | 0.48[f] | 0 | 7 | 40[g] | 98/2[e] |
| 3 | 1,3-cyclohexadiene | 0.092 | 0 | 8 | 60 | 99/1[e] |
| 4 | 1,3-cyclohexadiene | 0.098 | 20 | 7 | 75[h] | 98/2[e] |
| 5 | Isoprene | 0.47 | 0 | 8 | 63 | 100/0[i] |
| 6 | Isoprene | 0.49 | 20 | 7 | 54[j] | 98/2[i] |
| 7 | Dimethylbutadiene | 0.49 | 0 | 5 | 78 | – |

[a] Reactions were carried out in $CH_2Cl_2$ with 1.5 molar equivalents of diene.
[b] GC yield.
[c] Determined by GC.
[d] Isolated yield: 93%.
[e] Endo/exo.
[f] Regenerated catalyst.
[g] Yield after 66 h at 20 °C: 93%.
[h] Yield after 20 h: 90%.
[i] 1,4-disubstituted cyclohexene/1,3-disubstituted cyclohexene.
[j] Yield after 66 h: 68%.



Scheme 2. Formation of two regio-isomers in the Diels–Alder reaction of isoprene and methyl vinyl ketone.



Scheme 3. Structure of enones investigated in $H_3PW_{12}O_{40}$-catalyzed Diels–Alder reactions.

Table 2
Diels–Alder reactions of enones catalyzed by silica-supported $H_3PW_{12}O_{40}$.[a]

| Entry | Dienophile | Diene[b] | Cat. (mol%) | $T$ (°C) | $t$ (h) | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | Acrolein | CH | 0.37 | 0 | 5.5 | 82[d] |
| 2 | Acrolein | IP | 0.41 | 0 | 7 | 37[e] |
| 3 | Methacrolein | CH | 0.38 | 4 | 27 | 75[f] |
| 4 | Methyl acrylate | CP | 0.48 | 0 | 2 | 2 |

[a] Reactions were carried out in $CH_2Cl_2$ with 1.5 molar equivalents of diene.
[b] CH = 1,3-cyclohexadiene, IP = isoprene, CP = cyclopentadiene.
[c] GC yield.
[d] Endo/exo = 97 : 3.
[e] Only the 1,4-disubstituted cyclohexene derivative was observed.
[f] Endo/exo = 84 : 16.

The supported $H_3PW_{12}O_{40}$ catalyst was also applied to Diels–Alder reactions of MVK with the dienes 2,3-dimethylbutadiene and isoprene (scheme 2). The results are summarized in table 1 (entries 5–7). The yields of these reactions are lower than those of the reaction of MVK with 1,3-cyclohexadiene due to the more facile polymerization of these dienes compared to 1,3-cyclohexadiene. Moreover, depletion of the diene also leads to side-reactions of the dienophile. The extent of these side-reactions was reduced by performing the Diels–Alder reaction at a lower temperature (compare entries 5 and 6). Moreover, lowering the reaction temperature led to an increase in regioselectivity, e.g., isoprene afforded exclusively the 1,4-disubstituted cyclohexene at 0 °C.

To extend the scope of the $H_3PW_{12}O_{40}$-catalyzed Diels–Alder reactions, we investigated other dienophiles containing an acryl moiety (scheme 3) as substrate. The results are presented in table 2. The reaction of acrolein with 1,3-cyclohexadiene gave the adduct in 82% yield, which is comparable with the Nafion-H-catalyzed reaction [5], but the supported HPA showed a much higher activity. The reaction of acrolein and isoprene gave the adduct in lower yield. The reaction of methyl acrylate with cyclopentadiene showed almost no formation of the Diels–Alder adduct due to polymerization of the substrates. The same phenomenon was observed in the presence of the acid forms of zeolites [8].

The true heterogeneity of the supported $H_3PW_{12}O_{40}$ catalyst was established in the reaction between MVK and 1,3-cyclohexadiene. A reaction was performed at 0 °C in $CH_2Cl_2$ and the catalyst was filtered off after 5 min, which corresponded to 20% conversion. The filtrate was maintained at 0 °C for 2 h but no further reaction was observed.

Summarizing, tungstophosphoric acid supported on silica gel is an easily prepared, effective heterogeneous catalyst for Diels–Alder reactions of various enones under mild conditions and can be separated from the reaction mixture by simple filtration. The Diels–Alder adducts were formed in excellent regio- and stereoselectivity. With less reactive reaction partners the Diels–Alder reactions were accompanied by extensive polymerization of the diene and/or dienophile.

## 3. Experimental

### 3.1. Materials and methods

$^1$H-NMR spectra were measured in $CDCl_3$ as solvent and TMS as reference using a Varian VXR-400S spectrometer. Gas chromatography was performed with a Varian Star 3400 CX gas chromatograph with a CP Sil5 CB ($25\ \mathrm{m} \times 0.25\ \mathrm{mm}$) column. Column chromatography was performed over silica (Merck kieselgel 60, particle size 63–200 $\mu$m).

Aerosil 200 silica gel was purchased from Degussa, and tungstophosphoric acid and trifluoromethanesulfonic acid from Acros. All dienes and dienophiles were purchased from Aldrich and were freshly distilled before use. Dichloromethane was dried on molecular sieves 3A.

### 3.2. Catalyst preparation

Tungstophosphoric acid (40 wt%) on silica gel was prepared by impregnating Aerosil 200 by an aqueous solution of $H_3PW_{12}O_{40}$ followed by drying in a rotary evaporator. Prior to use, the supported HPA catalyst was pre-treated for 1.5 h at 130 °C/0.3 mm Hg.

### 3.3. Diels–Alder reactions

The dienophile (5–10 mmol) and decane (internal standard) were added to a suspension of the supported HPA in dichloromethane. The diene (1.5 equivalents) was added dropwise (syringe) to the stirred reaction mixture. The reactions were monitored by analyzing samples by gas chromatography. Diels–Alder adducts were isolated by column chromatography using dichloromethane as eluent.

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