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Heteropoly acid-catalyzed Diels–Alder reactions

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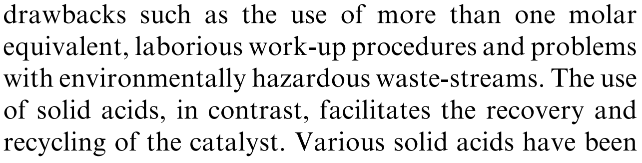
Tungstophosphoric acid supported on silica gel has been shown to catalyze Diels–Alder reactions of quinones. The catalyst is active under mild conditions and can be easily recovered and re-used.

Keywords: heteropoly acids, Diels–Alder reaction, heterogeneous catalysis

The Diels–Alder reaction is widely used in organic synthesis and several methods are known to enhance the rates of these reactions [1]. Lewis acids, for example, are frequently used as catalysts. However, they have serious drawbacks such as the use of more than one molar equivalent, laborious work-up procedures and problems with environmentally hazardous waste-streams. The use of solid acids, in contrast, facilitates the recovery and recycling of the catalyst. Various solid acids have been used as catalysts in Diels–Alder reactions, e.g. Nafion-H [2], clays [3], alumina [4], silica gel [5], silica and alumina modified by Lewis acids [6], zeolites [7], and synthetic $AlPO_4$ systems [8].

Heteropoly acids (HPA's) are polyoxometalates incorporating anions with metal–oxygen octahedra as the basic structural unit. Owing to their strong Brønsted acidity they are widely used as acid catalysts [9] but, to our knowledge, they have not been previously reported to catalyze Diels–Alder reactions.

Here we present the results of a study on Diels–Alder reactions of quinones heterogeneously catalyzed by the HPA, $H_3PW_{12}O_{40}$, both bulk and supported on silica gel. We found that $H_3PW_{12}O_{40}$ dramatically accelerates the Diels–Alder reaction of 1,4-naphthoquinone and 2,3-dimethylbutadiene:



With 5 mol% of $H_3PW_{12}O_{40}$ the conversion of the quinone was complete (TLC) within 20 h stirring at 20°C and the isolated yield of the Diels–Alder adduct was 70%. Under the same conditions the non-catalyzed reaction showed no conversion of the dienophile.

Because bulk HPA's have a low surface area (1–5 m^2/g) we also studied $H_3PW_{12}O_{40}$ supported on silica gel [10]. The latter catalyst has a much larger surface area and a greater number of accessible acid sites. Three $H_3PW_{12}O_{40}/SiO_2$ catalysts with various polyanion loadings (20, 30, and 40 wt%) were applied in the reaction of 1,4-naphthoquinone and 2,3-dimethylbutadiene (table 1, entries 2, 3, and 4). The 40 wt% catalyst showed the best performance. Complete conversion of the quinone was observed in 30 min and the Diels–Alder adduct was isolated in 75% yield. The results with the supported catalysts are summarized in table 1.

In a control experiment silica gel was applied as catalyst in the reaction of 1,4-naphthoquinone and 2,3-dimethylbutadiene. It took 120 h to reach only a conversion of about 75% with 2.5 wt% of silica gel. We also performed this Diels–Alder reaction with a regenerated catalyst (table 1, entry 8). After one run the precipitated catalyst was washed thoroughly with toluene and dried under reduced pressure. The re-used catalyst exhibited the same high activity.

On the basis of these results we performed the Diels–Alder reaction of 1,4-naphthoquinone and 2,3-dimethylbutadiene in the presence of two acidic salts of tungstophosphoric acid, $Ce_{0.87}H_{0.4}PW_{12}O_{40}$ [11] and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [12] (table 1, entries 12 and 13). The cerium salt showed the same catalytic activity as bulk $H_3PW_{12}O_{40}$ and the Diels–Alder adduct was obtained in 71% isolated yield. The cesium salt, in contrast, was virtually inactive.

In summary, we have demonstrated that tungstophosphoric acid supported on silica gel is an effective

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Table 1
Diels–Alder reactions catalyzed by silica-supported $H_3PW_{12}O_{40}$ [a]

Entry	Dienophile	Diene [b]	Mol% cat.	T (°C)	t[c] (h)	Yield[d]
1	1,4-naphthoquinone	DM	2 [e]	20	20	70
2	1,4-naphthoquinone	DM	2 [f]	20	0.75	69
3	1,4-naphthoquinone	DM	2 [g]	20	0.75	68
4	1,4-naphthoquinone	DM	2	20	0.5	75
5	1,4-naphthoquinone	DM	0.8	20	3	70
6	1,4-naphthoquinone	DM	0.2	20	20	67
7	1,4-naphthoquinone	DM	2	0	2	70
8	1,4-naphthoquinone	DM	2 [h]	20	0.75	72
9	1,4-naphthoquinone	CH	2	20	2	78
10	toluquinone	DM	2	20	2	70
11	benzoquinone	DM	2	20	2	60
12	1,4-naphthoquinone	DM	2 [i]	20	20	71
13	1,4-naphthoquinone	DM	2 [j]	20	20	– [k]

[a] Unless otherwise stated reactions were carried out in toluene with 1.5 molar equivalents of diene in the presence of 40 wt% $H_3PW_{12}O_{40}$ supported on SiO_2.

[b] DM = 2,3-dimethylbutadiene, CH = 1,3-cyclohexadiene. [c] Time for complete conversion of dienophile.

[d] The yields of isolated adducts are given. [e] Bulk HPA. [f] 20 wt% of $H_3PW_{12}O_{40}$ on SiO_2 was used. [g] 30 wt% of $H_3PW_{12}O_{40}$ on SiO_2 was used.

[h] Regenerated catalyst. [i] With $Ce_{0.87}H_{0.4}PW_{12}O_{40}$. [j] With $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. [k] No detectable formation of Diels–Alder adduct.

heterogeneous catalyst for Diels–Alder reactions of quinones. The catalyst is active under mild conditions, is simply separated from the reaction mixture and can be easily recovered and re-used. The HPA catalysts are significantly more efficient than conventional solid acid catalysts such as silica and silica–alumina. Even Nafion-H, a perfluorinated resinsulfonic acid and comparable in its strength to 100% sulfuric acid, is less active (on the basis of the weight) than $H_3PW_{12}O_{40}$ on SiO_2. Future studies will focus on the use of HPA's as catalysts for Diels–Alder reactions with other dienophiles and their utility in other carbon–carbon bond forming reactions.

Experimental

Materials. Aerosil 200 silica gel was purchased from Degussa, tungstophosphoric acid from Acros, and 1,4-naphthoquinone (> 99%) from Fluka. 1,3-cyclohexadiene and 2,3-dimethylbutadiene were purchased from Aldrich and freshly distilled before use.

Catalyst preparation. 20, 30, and 40 wt% $H_3PW_{12}O_{40}/SiO_2$ were 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 both bulk and supported HPA catalysts were pre-treated at 130°C/0.3 mm Hg for 1.5 h.

Diels–Alder reactions. The quinone (0.25 g) and the diene (1.5 equiv.) were added to a suspension of the supported HPA (0.22 g, 2 mol% on quinone) in toluene (10 ml). The mixture was stirred until TLC (eluent dichloromethane/acetone 98 : 2) showed complete conversion of the quinone (see indicated times in table 1). The catalyst was filtered off and toluene evaporated under vacuum. The residue was recrystallized from methanol and petroleum ether 1 : 1 (v/v) (Diels–Alder adducts of 1,4-naphthoquinone) or petroleum ether (adducts of toluquinone and benzoquinone). The structures of the Diels–Alder adducts were confirmed by ^1H and ^{13}C NMR.

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