Supporting information for:

Calcium Tungstate: A Convenient Recoverable Catalyst for Hydrogen Peroxide Oxidation

Catlin M. Williamson, Peter Stonehouse and Keith S. Kyler*

Address: Department of Chemistry, Indiana University of Pennsylvania, Indiana, Pennsylvania, 15707

Keith.kyler@iup.edu

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1. General Procedure for the Oxidation of Amines: To 2.2 L of 30% H$_2$O$_2$ (12.4 mol) was added 3.4 g (0.12 mol) of CaWO$_4$. The mixture was warmed to 45 ºC and the solid dissolved to produce a yellow solution. Then was added dropwise over a 30 min period, 1 kg (2.3 mol) of p-toluidine while maintaining the temperature below 50 ºC. After complete addition, the mixture was warmed to 95 ºC for about 1 h at which point the yellow color of the aqueous phase disappeared and the colorless CaWO$_4$ precipitated. The mixture was cooled to room temperature, and the organic phase was separated and distilled to afford 1.1 kg (98%) of p-nitrotoluene, whose $^1$H-NMR and IR spectra were consistent with reported data. The aqueous phase was filtered and the CaWO$_4$ (3.4g, >99%+) was recovered.

2. General Procedure for the Oxidation of Alkenes. To 45.0 mL of 30% H$_2$O$_2$ (0.4 mol) and 45 mL of t-butanol was added 0.288 g (1 mmol) of CaWO$_4$. The mixture was warmed to 45 ºC and the solid dissolved to produce a yellow solution. Then was added 9.4 g (0.10 mol) of norbornene and the mixture was stirred vigorously for 4h at 65 ºC. The mixture was then warmed to 95 ºC for approximately 10 min at which point the yellow color of the aqueous phase disappeared and the colorless CaWO$_4$ precipitated. The mixture was cooled to room temperature, and organic product was extracted with ethyl acetate. The organic phase was dried over anhydrous MgSO$_4$, and evaporated to afford 10.55 g (98%) of exo-2,3-epoxynorbornane ($^5$). $^1$H-NMR (CDCl$_3$) d 0.92 (2H, d), 1.32 (4H, d), 2.20 (2H, br s) and 3.18 (2H, br s). Decoupled $^{13}$C-NMR (CDCl$_3$) d 24.4, 25.5, 34.2, 51.0. The aqueous phase was filtered and the CaWO$_4$ (0.287g, 99%+) was recovered.

3. General Procedure for the Oxidation of Alcohols. To 453 mL of 30% H$_2$O$_2$ (4.0 mol) and 400 mL of methanol was added 2.88 g (0.01 mol) of CaWO$_4$. The mixture was warmed to 45 ºC and the solid dissolved to produce a yellow solution. Then was added 100 g (1.0 mol) of cyclohexanol and the mixture was stirred vigorously for 20 h at 65 - 70 ºC. The mixture was then warmed to 95 ºC for approximately 1 h at which point the yellow color of the aqueous phase disappeared and the colorless CaWO$_4$ precipitated. The mixture was cooled to room temperature, and organic layer was separated and distilled to afford 95 g (97%) of cyclohexanone, ($^6$), bp 152-156 ºC, lit., 156 ºC.

4. General Procedure for the Oxidation of sulfides. To 22 mL of 30% H$_2$O$_2$ (0.20 mol) and 20 mL of t-butanol was added 0.288 g (0.001 mol) of CaWO$_4$. The mixture was warmed to 45 ºC and the solid dissolved to produce a yellow solution. The mixture was then cooled to 25 ºC, and was added 15.2 g (0.1 mol) of isopropylphenyl sulfide. The mixture was stirred vigorously for 0.5 h at 25 ºC. The mixture was then warmed to 95 ºC for approximately 1 h at which point the yellow color of the aqueous phase disappeared and the colorless CaWO$_4$ precipitated. The mixture was cooled to room temperature, and 50 mL of ethyl acetate was added then the organic layer was separated and dried over anhydrous MgSO$_4$. Evaporation gave a crude colorless solid which was titurated with cold hexane, filtered, then dried to afford 17.7 g (96%)= of a colorless solid, ($^10$). IR (KBr) 3094, 2977, 1305, 1144, and 730 cm$^{-1}$. GC-MS; 184 (M$^+$), 142 (78), 78 (100), 51 (22), 43 (36).
5. **UV-Visible Spectra for Tungstate Solutions:** All spectra were recorded at 25 °C on a double-beam Perkin-Elmer Model 552A UV/Vis Spectrophotometer using either water or H$_2$O$_2$(aq) as blanks where appropriate. Data were recorded between 500 – 190 nm.

a) 1.0 mM Na$_2$WO$_4$ in water

b) 1.0 mM Na$_2$WO$_4$ in 8% H$_2$O$_2$
c) 1.0 mM CaWO$_4$ in 8% H$_2$O$_2$
6. Photographs and IR Spectra of CaWO₄ before and after Five cycles of Oxidation

a) CaWO₄ prior to oxidations

b) CaWO₄ after five cycles of oxidations
c) Overlay of IR Spectra of CaWO$_4$ before (A) and after (B) five cycles of oxidation
7. All NMR spectra were obtained on a Bruker 300 MHz spectrometer. All Infrared spectra were obtained on a Perkin Elmer Frontier FTIR.

Nitrobenzene: $^1$H-NMR (CDCl$_3$)
Nitrobenzene: $^{13}$C-NMR (CDCl$_3$)
Nitrobenzene: IR
4-nitrotoluene: $^1$H-NMR (CDCl$_3$)
4-nitrotoluene: $^{13}$C-NMR (CDCl$_3$)
3-nitroisoxazole: $^1$H-NMR (CDCl$_3$)
3-nitroisoxazole: $^{13}$C-NMR (CDCl$_3$)
Cyclohexene oxide: $^1$H-NMR (CDCl$_3$)
Cyclohexene oxide: $^{13}\text{C}-\text{NMR (CDCl}_3)$
Exopxynorbornane: $^1$H-NMR (CDCl$_3$)
Epoxynorbonane: $^{13}$C-NMR (CDCl$_3$)
Epoxynorbornane: IR

[Graph of infrared spectrum with labeled peaks and wavelengths]
Cyclohexanone: $^1$H-NMR (CDCl$_3$)
Cyclohexanone: $^{13}$C-NMR (CDCl$_3$)
Cyclohexanone: IR
3-pentanone: $^1$H-NMR ($\text{CDCl}_3$)
3-pentanone: $^{13}$C-NMR (CDCl$_3$)
3-pentanone: IR

[Graph and table data]

3-pentanone

[Chemical structure image]
2,3-Epoxygeraniol: $^1$H-NMR (CDCl$_3$)
2,3-Epoxygeraniol: $^{13}$C-NMR (CDCl$_3$)
Ethylphenylsulfone: $^1$H-NMR (CDCl$_3$)
Ethylphenylsulfone: $^{13}$C-NMR (CDCl$_3$)
Ethylphenylsulfone: IR
Isopropylphenylsulfone: $^1$H-NMR (CDCl$_3$)
Isopropylphenylsulfone: $^{13}$C-NMR (CDCl$_3$)
Isopropylphenylsulfone: IR