



Supporting Information

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Formation of S-Shaped Disilicoeicosatungstate (W_{20}) and the Efficient Baeyer-Villiger Oxidation with Hydrogen Peroxide

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Experimental details

Instruments. IR measurements were carried out as KBr pellets using JASCO FT/IR-460 plus spectrometer. NMR spectra were recorded at room temperature on JEOL JNM-EX-270 (1H , 270.0 MHz; ^{13}C , 67.8 MHz) spectrometer. Chemical shifts (δ) were reported in ppm downfield from internal $SiMe_4$. UV-vis spectra were recorded on a Perkin Elmer Lambda 12 spectrometer. Gas chromatographic (GC) analysis was carried out on a Perkin Elmer Autosystem GC equipped with a TC-WAX column (30 m, 0.25 mmID, 0.25 μmdf ; GL-Science).

Materials and Methods. The solvents (acetonitrile and 1,2-dichloroethane) used for the syntheses of the silicotungstates were dried with P_2O_5 , distilled, and stored under argon. Nitromethane (Tokyo Kasei Kogyo Co., Ltd.; 98.0 %) for the catalytic reactions was used as received. The commercially available reagents of the highest grade were used without further purification. The starting material of the silicotungstate, $K_8[SiW_{10}O_{36}] \cdot 8H_2O$ ($K_8 \cdot [1'] \cdot 8H_2O$), was prepared according to the reported method.^[1]

Synthesis of tetra-*n*-butylammonium salt of $[g-SiW_{10}(H_2O)_2O_{34}]^{4-}$ ($TBA_4 \cdot [1]$). The non-protonated silicodecatungstate, $[\gamma-SiW_{10}O_{36}]$ ($1'$), was purified by the cation exchange method: The potassium salt of $1'$ ($K_8 \cdot [1'] \cdot 8H_2O$; 12.2 g, 4.7 mmol) was dissolved in 240 mL of H_2O . The addition of $RbCl$ (1.50 g, 12.5 mmol) to this solution resulted in the white precipitate of impurities and then the impurities were

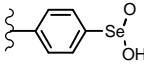
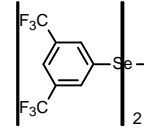
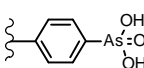
removed by the filtration. The evaporation of the filtrate yielded white solids of Rb salt of **1'**. The obtained Rb salt of **1'** (3.5 g, 1 mmol) was dispersed in 35 mL of water and then the pH of this aqueous solution was adjusted to 2 with 20 % HNO₃. After stirring the resulting clear solution for 5 min at room temperature, an excess amount of [(*n*-C₄H₉)₄N]Br (1.48 g, 1.15 mmol) was added in a single step. The resulting white precipitate was collected by the filtration and then washed with an excess amount of H₂O (three times). An analytically pure white powder of TBA₄·[**1**] was obtained by the evacuation to dryness at room temperature.

Checking the effect of CF₃SO₃⁻ on the catalytic activity of **2.** The ¹⁹F NMR analysis revealed that a small amount of the TBA salt of CF₃SO₃⁻ (< 0.8 mol % of **2**) was contained in the crystalline solid of as-prepared catalyst **2**. We confirmed that the presence of CF₃SO₃⁻ did not affect the BV oxidation of cyclopentanone as follows: The reaction rate with **2** was not changed by the addition of TBA·CF₃SO₃ (10 mol % of **2**). In addition, we carried out the control experiment by using 0.005 mol % of CF₃SO₃H instead of 0.5 mol % of **2** with respect to H₂O₂ (the amount of CF₃SO₃H corresponded to the 1 mol % of **2**). The initial rate for CF₃SO₃H (4.97 × 10⁻² mM·min⁻¹) was almost 10³ times smaller than that for **2** (49.5 mM·min⁻¹). Therefore, the effect of the contaminated CF₃SO₃⁻ (or CF₃SO₃H) on the oxidation catalysis is negligible.

Reference for supporting information

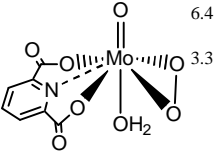
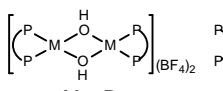
- (1) A. Tézé, G. Hervé, *Inorg. Synth.* **1990**, 27, 85.

Table S-1: Reported catalytic Baeyer-Villiger oxidation with H₂O₂.

Catalyst	Amount of catalyst [mol%]	H ₂ O ₂ conc. [%]	Ketone	Ratio of H ₂ O ₂ /Ketone	Yield [%]	Selec. efficiency [%]	H ₂ O ₂ [%]	TON	Solvent	Temp. [K]	Time	ref.
	1.46	30	cyclopentanone	1.8	98	-	54	67	CH ₂ Cl ₂	298	72 h	[1]
			2-methylcyclopentanone		86	-	48	59		298	103 h	[1]
			cyclobutanone		96	-	53	66		298	3 h	[1]
			2,6-dimethylcyclohexanone		92	-	51	63		298	108 h	[1]
	0.5	60	cyclobutanone	2.0	89	90	45	178	CF ₃ CH ₂ OH	293	1 h	[2]
			cyclopentanone		89	94	45	178		293	8 h	[2]
			cyclohexanone		94	99	47	188		293	4 h	[2]
			2-adamantanone		99	99	50	198		293	1 h	[2]
	3.2	90	cyclohexanone	0.2	63	80	80	20	Dioxane	353	7 h	[3]
			2-methylcyclohexanone		78	100	100	24		353	5 h	[3]
			cyclopentanone		79	85	79	24		353	8 h	[3]
			cyclobutanone		98	100	100	30		353	0.5 h	[3]
Sn/Hydrotalcite Sn = 1.5 wt%	0.26	30	cyclohexanone	4	26	100	6.5	102	MeCN	343	4 h	[4]
			2-methylcyclohexanone		42	100	11	164		343	4 h	[4]
			3-methylcyclohexanone		32	100	8.0	125		343	4 h	[4]
			4-methylcyclohexanone		26	100	6.5	102		343	4 h	[4]
			cyclopentanone		16	100	4.0	63		343	4 h	[4]
Sn-zeolite beta Sn = 1.5 wt%	1.0	30	cyclohexanone	0.67	52	>98	52	52	Dioxane	363	3 h	[5]
	0.67		2-adamantanone	1	94	>98	94	140	MTBE	329	6 h	[5]
<i>p</i> -TsOH	1.0	50	cyclohexanone	1.3	92	>99	71	92	(CF ₃) ₂ CHOH	333	40 min	[6]
Amberlyst 15	-	30	cyclopentanone	1.5	66	69	44	-	solventless	343	6 h	[7]
H-ZSM-5	-	30	cyclopentanone	ca. 5	15	32	ca. 3	-	1,2-DCE	313	5 h	[8]

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Table S-1 (continued)

Catalyst	Amount of catalyst [mol%]	H ₂ O ₂ conc. [%]	Ketone	Ratio of H ₂ O ₂ /Ketone	Yield [%]	Selec. efficiency [%]	H ₂ O ₂ [%]	TON	Solvent	Temp. [K]	Time	ref.
CH ₃ ReO ₃	6.4	?	cyclobutanone	2.7	80	100	30	13	MeCN	298	12 h	[9]
			cyclopentanone		15	75	5.6	2.3		298	72 h	[9]
			cyclohexanone		21	100	7.8	3.3		298	72 h	[9]
			methylcyclohexanone		20	61	7.4	3.1		298	72 h	[9]
CH ₃ ReO ₃	0.3	3.0 M Et ₂ O soln.	cyclobutanone derivatives	2.2	63-80	-	29-36	210-267	Et ₂ O	293	1-24 h	[10]
CH ₃ ReO ₃ /[bmim]BF ₄	2.0	50	cyclobutanone	2	>98	>99	>49	>49	MeCN	r.t.	1 h	[11]
			cyclopentanone	6	70	<71	12	35		333	24 h	[11]
			2-methylcyclopentanone	6	75	<77	13	38		333	24 h	[11]
			3-methylcyclopentanone	6	74	82	12	37		333	24 h	[11]
			cyclohexanone	6	20	50	3.3	10		333	48 h	[11]
			2-methylcyclohexanone	6	20	53	3.3	10		333	48 h	[11]
			3-methylcyclohexanone	6	18	50	3.0	9.0		333	48 h	[11]
			2-Adamantanone	4	>98	>99	>25	>49		333	12 h	[11]
	6.4	70	cyclopentanone	1.6	35	54	43	5.5	MeCN	343	9 h	[12]
	3.3	90	cyclopentanone	1	40	95	40	12	MeCN	333	24 h	[13]
			2-methylcyclopentanone		82	95	82	25		333	24 h	[13]
			cyclohexanone		10	100	10	3.0		333	24 h	[13]
			2-methylcyclohexanone		10	47	10	3.0		333	24 h	[13]
												
M = Pt	10	60	2-methylcyclohexanone	1	55	-	55	5.5	1,2-DCE	298	5 h	[14]
M = Pd	10	60	2-methylcyclohexanone	1	4.9	-	4.9	0.49		298	1 h	[14]

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