

Polyoxometalates

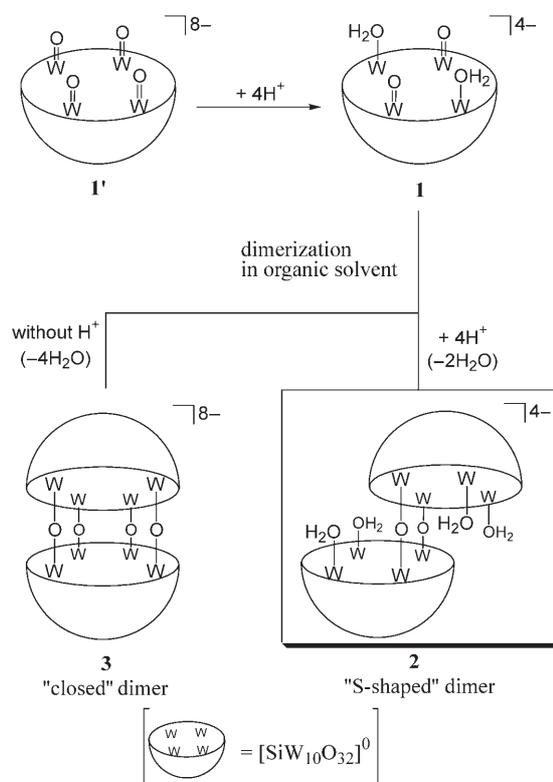
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Formation of S-Shaped Disilicoicosatungstate and Efficient Baeyer–Villiger Oxidation with Hydrogen Peroxide**

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Metal–oxygen clusters, namely, polyoxometalates (POMs), have attracted much attention because of their tunability of composition, size, shape, acid–base properties, and redox potential.^[1] The molecular properties lead to the use of POMs in catalysis, medicine, and materials science. Structural variations of POMs may arise from self-assembly of M–O/M–OH components and from isomerization by repetitive hydrolysis and condensation of metal fragments in aqueous media, and these behaviors complicate POM chemistry.^[2] Therefore, synthesis, structural characterization, and chemical properties of novel POMs are still attractive in modern chemistry. Lacunary POMs are useful precursors for mixed-metal–oxide clusters and organic–inorganic hybrid compounds.^[1] Especially the γ isomer of a divacant Keggin-type silicododecatungstate, namely, $[\text{SiW}_{10}\text{O}_{36}]^{8-}$ (**1'**),^[3] has been used as a molecular replica to synthesize dimetal-substituted POMs with reactive dinuclear $\text{M}_2(\mu\text{-O})_2$ sites.^[4] We have also synthesized aqua-ligated divacant silicododecatungstate

$[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ (**1**) by treatment of **1'** with H^+ in aqueous solution at pH 2 (Scheme 1).^[5] Single-crystal X-ray structure analysis of **1** indicates that two of four oxo ligands located at the vacant sites are selectively protonated to give the aquatungsten moieties.



Scheme 1. Formation of disilicoicosatungstates **2** and **3**.

Baeyer–Villiger oxidation is well known and widely used in organic synthesis because of its versatility, although it is carried out with expensive and/or hazardous peracids and leads to formation of one equivalent of the corresponding carboxylic acid. Therefore, efforts have been made to develop homogeneous and heterogeneous catalytic systems with hydrogen peroxide or organic peracids generated by the reaction of either the corresponding aldehyde with dioxygen or the carboxylic acid with hydrogen peroxide.^[6] Herein we report novel disilicoicosatungstates $[\{\gamma\text{-SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\mu\text{-O})_2]^{4-}$ (**2**) and $[\{\gamma\text{-SiW}_{10}\text{O}_{32}\}_2(\mu\text{-O})_4]^{8-}$ (**3**), formed by dimerization of **1** by dehydrative condensation in an organic solvent. Interestingly, **2** can catalyze the Baeyer–Villiger oxidation of cycloalkanones with H_2O_2 and shows high selectivity ($\geq 90\%$) for the corresponding lactones and high turnover numbers (≥ 1900), whereas **1** and **3** with the common $[\gamma\text{-SiW}_{10}\text{O}_{32}]$ fragment are almost inactive.

The tetra-*n*-butylammonium salt of **1** ($(\text{TBA})_4[\mathbf{1}]$) was transformed to the TBA salt of **2** (Scheme 1 and Experimental Section). The IR spectrum of **2** was clearly different from that of **1**, and this suggested a structural change of the cluster framework. The molecular structure of **2** was determined by X-ray analysis on a colorless single crystal. As shown in Figure 1 a, **2** has an S-shaped molecular structure composed of

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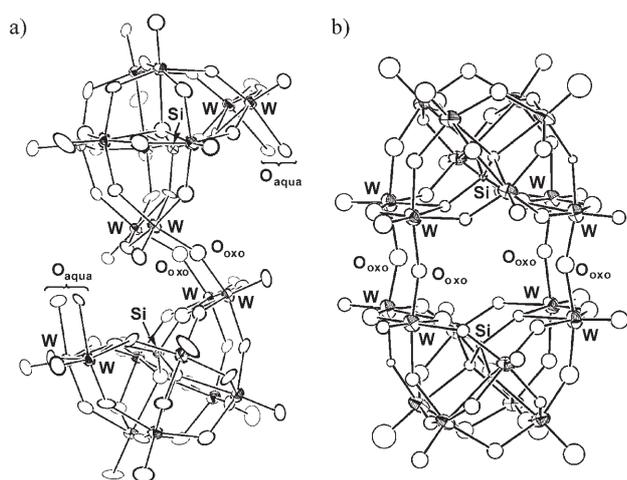


Figure 1. Molecular structures of **2** (a) and **3** (b). The thermal ellipsoid probabilities for **2** and **3** are shown at 30 and 50%, respectively.

two neutral divacant γ -Keggin-type $[\text{SiW}_{10}\text{O}_{32}]^0$ fragments bridged by two oxo ligands. The four unbridged W sites are occupied by aqua ligands ($\text{W}-\text{O}_{\text{aqua}}$ 2.19(3)–2.22(3) Å, $\text{W}=\text{O}_{\text{oxo}}$ 1.62(2)–1.81(3) Å). In other words, **2** is a dimer of the $[\text{SiW}_{10}\text{O}_{33}(\text{H}_2\text{O})_2]^{2-}$ fragment and was formed by the loss of one oxo ligand of **1** by protonation followed by dissociation as water.^[7]

It is known that one of two terminal oxo ligands in dioxo complexes of d^0 metals (V^{V} , Mo^{VI} , W^{VI}) is basic enough to react with various protic substrates, and the ligand-exchange reaction then proceeds through dissociation of the protonated oxo (i.e., aqua) ligand. Indeed, several organic-modified POMs have been synthesized by reaction of the $\text{W}(\text{=O})_2$ moieties of divacant silicodecatungstate **1'** (unprotonated form of **1**) with protic substrates such as silanols and phosphoric acids.^[8] In these organic-modified compounds, however, the tungsten sites are fully occupied. In contrast, **2** retains four vacant sites (terminal $\text{W}(\text{=O})(\text{OH}_2)$ moieties). It is notable that the divacant γ -Keggin framework of the $[\text{SiW}_{10}\text{O}_{32}]$ fragment of **1** remained unchanged in **2** in spite of the action of strong acid in an aprotic organic solvent during its formation. To date, a sole example of an icosatungstate, namely, $[\text{KP}_2\text{W}_{20}\text{O}_{72}]^{13-}$, has been reported: This diphosphoicosatungstate is composed of two $[\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ fragments bridged by two octahedral WO_6 units and K^+ , and therefore the structure is clearly different from those of **2** (S-shaped) and **3** ("closed" cluster; see Figure 1 b and below).^[9]

In the absence of H^+ , another type of disilicoicosatungstate **3** was formed by dimerization of **1** (Scheme 1 and Experimental Section). The IR spectrum of **3** was different from those of **1** and **2**, whereas the elemental analyses indicated that the Si:W ratios were all 1:10. Single-crystal X-ray structure analysis of the $[\text{K}(\text{[18]crown-6})]^+$ salt revealed that **3** is a "closed" dimer of the $[\text{SiW}_{10}\text{O}_{34}]^{4-}$ fragment (Figure 1 b), formed by dissociation of aqua ligands from **1**.^[10]

The Baeyer–Villiger oxidation of cyclopentanone with H_2O_2 was carried out in the presence of S-shaped dimeric cluster **2**. Oxidation was quantitatively complete after 45 min and the selectivity for δ -valerolactone (**4**) and the efficiency

of H_2O_2 utilization were 99% or higher. The yield of **4** from the oxidation of cyclopentanone in MeCN was 96%, almost the same as that in MeNO₂. The yield of **4** from the oxidation of cyclopentanone with 30% aqueous H_2O_2 in MeNO₂ was 91%. The catalytic activity of **2** was compared with those of **1** and **3** (Table 1). The S-shaped cluster **2** catalyzed the reaction

Table 1: Comparison of the catalytic activities of **1**, **2**, and **3** in the oxidation of cyclopentanone.

| Catalyst | Initial rate [$\text{mM}^{-1} \text{min}^{-1}$] | Conversion [%] | Selectivity for 4 [%] | Yield of 4 [%] |
|----------|--|----------------|---------------------------------|--------------------------|
| 1 | 0.082 | 2 | ≥ 99 | 2 |
| 2 | 49 | ≥ 99 | ≥ 99 | ≥ 99 |
| 3 | 0.13 | 4 | ≥ 99 | 4 |

well, whereas monomeric precursor **1** and closed dimer **3** exhibited quite low activities: the initial rate for **2** (49 mM min^{-1}) was more than 100 times larger than those for **1** (0.082) and **3** (0.13). Thus, the catalytic activities of **1**–**3** are different, although they all are composed of common $[\gamma\text{-SiW}_{10}\text{O}_{32}]$ fragments. Peroxotungstates such as $[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ and $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ were almost inactive under the present reaction conditions. The S-shaped cluster **2** is the first example of a tungsten catalyst for Baeyer–Villiger oxidation with high selectivity for the lactone, high efficiency of H_2O_2 utilization, and high turnover number.^[11,12] Catalyst **2** is stable under the reaction conditions: the UV/Vis and IR spectra of the recovered catalyst were the same as those of the as-prepared one. The reusability of catalyst **2** was also confirmed by maintenance of activity for the oxygenation of cyclobutanone in repetitive reactions [yields of lactone: $\geq 99\%$ (first run), 98% (second run), 99% (third run)].

Table 2 summarizes the results for the Baeyer–Villiger oxidation of various cycloalkanones catalyzed by **2** ($\text{2:H}_2\text{O}_2\text{:substrate} = 1:200:1000$). Cyclobutanone, cyclopentanone, and 2-adamantanone were quantitatively converted into the corresponding lactones. Even in the oxidation of cyclobutanone and 2-adamantanone under stoichiometric conditions ($\text{H}_2\text{O}_2\text{:substrate} = 1:1$), the yields and selectivities for the corresponding lactones exceeded 95 and 99%, respectively. Acetophenone, which is hard to oxidize, was also converted to the corresponding ester and the hydrolysis products (phenol and benzoic acid).^[13,14] The regioselectivity of the oxygenation of 2-methylcyclopentanone depends on the direction of insertion of the oxygen atom.^[15] The **2**-mediated oxygenation of 2-methylcyclopentanone afforded δ -methyl- δ -valerolactone: α -methyl- δ -valerolactone = 64:36, and the ratio was clearly different from that observed for stoichiometric oxygenation with *m*-chloroperbenzoic acid (96:4).

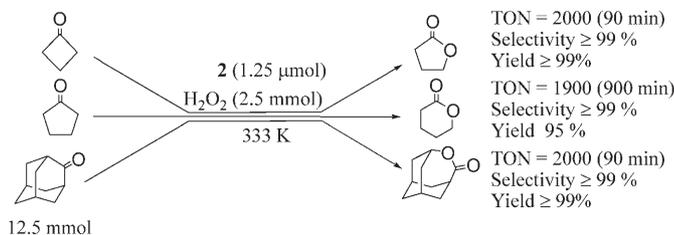
Larger-scale (tenfold scaleup) reactions with cyclobutanone, cyclopentanone, and 2-adamantanone exhibited turnover numbers (based on **2**) of 2000, 1900, and 2000, respectively (Scheme 2). These values are much higher than

Table 2: Baeyer–Villiger oxidation of cycloalkanones and acetophenone with H₂O₂ catalyzed by **2**.^[a]

| Substrate | Product(s) | Reaction time [min] | Conversion [%] | Selectivity for lactone(s) [%] | Yield [%] (Ratio of products) | TON (based on 2) |
|-----------|------------|---------------------|----------------|--------------------------------|-------------------------------|--------------------------|
| | | 5 | ≥ 99 | ≥ 99 | ≥ 99 | 200 |
| | | 45 | ≥ 99 | ≥ 99 | ≥ 99 | 200 |
| | | 45 | 70 | 90 | 63 (64:36) | 126 |
| | | 15 | ≥ 99 | ≥ 99 | ≥ 99 | 200 |
| | | 135 | 17 | 87 ^[b] | 15 (40:33:27) | 30 |

R = COOH, OH, OAc

[a] Reaction conditions: Catalyst (**2**), 1.25 μmol; substrate, 1.25 mmol; H₂O₂ (80% aqueous), 0.25 mmol; solvent (MeNO₂), 1.0 mL; reaction temperature, 333 K. Conversion, selectivity, and yield were determined by gas chromatography or ¹H NMR spectroscopy with an internal standard and are based on H₂O₂. [b] Selectivity for the ester and the successive hydrolysis products.



Scheme 2. Larger-scale Baeyer–Villiger oxidations with **2** as catalyst.

those reported for Baeyer–Villiger oxidations with H₂O₂ and other catalysts:^[6,13,15–18] for cyclobutanone: [Pt^{II}(CF₃)(dppe)-(CH₂Cl₂)](BF₄) (dppe = 1,4-bis(diphenylphosphanyl)ethane), TON = 333,^[6b] bis[3,5-bis(trifluoromethyl)phenyl] diselenide (TON = 178),^[18b] for 2-adamantanone: Sn-beta zeolite (TON = 140),^[13a] bis[3,5-bis(trifluoromethyl)phenyl] diselenide (TON = 198).^[18b]

In conclusion, dehydrative condensation of [SiW₁₀O₃₄-(H₂O)₂]⁴⁻ (**1**), which was obtained by partial protonation of [SiW₁₀O₃₆]⁸⁻ (**1'**), yielded the novel disilicoicosatungstates [[γ-SiW₁₀O₃₂(H₂O)₂]₂(μ-O)₂]⁴⁻ (**2**; S-shaped cluster) and [(γ-SiW₁₀O₃₂)₂(μ-O)₄]⁸⁻ (**3**; closed cluster). The S-shaped cluster **2** was selectively obtained in the presence of H⁺ during the dimerization reaction. Baeyer–Villiger oxidation of cycloalkanones to give the corresponding lactones with H₂O₂ was efficiently catalyzed by **2** (≥ 90% selectivity for the lactone and TON ≥ 1900), whereas monomeric precursor **1** and closed cluster **3** exhibited very low activity.

Experimental Section

(TBA)₄[**2**]: (TBA)₄[**1**] (0.99 g, 0.29 mmol) was dissolved in 1,2-dichloroethane (10 mL) and CF₃SO₃H (80 μL, 0.60 mmol) was added. The insoluble solids were removed by filtration. The solution was kept at 293 K for one week to afford colorless rodlike crystals of (TBA)₄[**2**] (0.71 g, 85% yield). Elemental analysis (%) calcd for

(TBA)₄[**2**]: C 13.18, H 2.63, N 0.96; found: C 13.46, H 2.78, N 0.97. IR (KBr): $\tilde{\nu}$ 2963 (m), 2934 (w), 2874 (m), 1483 (m), 1470 (sh), 1380 (m), 974 (s), 931 (sh), 915 (s), 879 (s), 817 (sh), 794 (s), 741 (sh), 676 (s), 557 (m), 412 (w), 386 (w), 363 (m), 332 (w), 303 cm⁻¹ (w). UV/Vis (MeCN): λ = 265 nm (sh; ϵ = 57920 M⁻¹cm⁻¹). Because of the extremely low solubility of **2**, its ¹⁸³W and ²⁹Si NMR spectra in solution could not be measured.

TBA salt of **3**: (TBA)₄[**1**] (3.00 g, 0.88 mmol) was dissolved in 1,2-dichloroethane (30 mL) and the resulting solution was stirred under Ar for 72 h at ambient temperature. After the removal of a small amount of insoluble solids by filtration, the filtrate was evaporated to dryness under reduced pressure. Part of the resulting pale yellow solid (0.81 g) was dissolved in 1,2-dichloroethane (2.4 mL) and benzene (0.6 mL) was added. Pale yellow crystals of the TBA salt of **3** (0.39 g,

0.06 mmol) precipitated on allowing the solution to stand for one week at 293 K. Elemental analysis (%) calcd for (TBA)₄H[**3**]·6C₂H₄Cl₂: C 20.94, H 3.93, N 1.38; found: C 20.75, H 4.02, N 1.38. IR (KBr): $\tilde{\nu}$ 2960 (m), 2934 (w), 2874 (m), 1483 (m), 1470 (sh), 1380 (m), 1152 (w), 1107 (w), 1021 (m), 1001 (m), 959 (s), 930 (s), 901 (s), 872 (s), 789 (s), 755 (sh), 690 (w), 549 (m), 408 (w), 390 (w), 366 (m), 345 (w), 334 (w), 325 (w), 309 (w), 295 cm⁻¹ (w). UV/Vis (MeCN): 295 nm (sh; ϵ = 39640 M⁻¹cm⁻¹).

X-ray crystallography: Single crystals of (TBA)₄[**2**]·5H₂O were obtained as follows: (TBA)₄[**1**] (0.44 g, 0.12 mmol) was dissolved in nitromethane (2.0 mL), and CF₃SO₃H (19 μL, 0.24 mmol) was added. The solution was kept at 293 K. Colorless crystals were obtained over several hours. The single crystals were collected by filtration and washed with nitromethane (0.5 mL). The yield of (TBA)₄[**2**]·5H₂O was 0.14 g (40%). Crystals of the [K([18]crown-6)]⁺ salt of **3** were prepared as follows: K₈[**1'**]·12H₂O (2.98 g, 1.00 mmol) was dissolved in water (15 mL) and then the pH of this aqueous solution was adjusted to 2 with 2M HNO₃. After stirring this clear solution for 2 min at room temperature, [18]crown-6 (1.062 g, 4 mmol) was added in a single portion. The resulting pale yellow suspension was stirred for 5 min followed by evaporation to dryness to give 1.61 g of a pale yellow powder. A small amount of powder (58 mg) was suspended in MeCN (2.0 mL) and the insoluble solids were removed by filtration. Pale yellow crystals of [K([18]crown-6)]₆H₂[**3**]·8MeOH·8H₂O formed in the presence of MeOH vapor at ambient temperature.

Diffraction measurements were made on a Rigaku Saturn CCD detector with graphite-monochromated MoK α radiation (λ = 0.71069 Å; 5 kW). Data were collected and processed with CrystalClear (Rigaku). Neutral scattering factors were obtained from the standard source. In the data reduction, corrections for Lorentzian and polarization effects were made. Structural analyses were performed by using the CrystalClear crystallographic structure-solving program package. The structures were solved by heavy-atom Patterson methods and expanded by Fourier techniques. For (TBA)₄[**2**]·5H₂O, the tungsten, silicon, and oxygen atoms of **2** and the nitrogen atoms of the TBA ions were refined anisotropically in the final cycle of full-matrix least-squares refinement on *F*. The carbon atoms of one of the four TBA ions and the oxygen atoms of the water molecules were refined isotropically. The positions of the carbon atoms of the remaining disordered TBA ions were fixed, although the isotropic thermal parameters were refined. The hydrogen atoms of the isotropically refined TBA ion were located by using riding models.

For $[\text{K}(\text{[18]crown-6})]_6\text{H}_2\cdot 3\cdot 8\text{MeOH}\cdot 8\text{H}_2\text{O}$, the tungsten atoms were refined anisotropically, and the other atoms, except for one oxygen atom, were refined isotropically. The hydrogen atoms of the [18]crown-6 ligands were located by using riding models.

Crystal data for $(\text{TBA})_4[\mathbf{2}]\cdot 5\text{H}_2\text{O}$: $\text{C}_{64}\text{H}_{160}\text{N}_4\text{O}_{75}\text{Si}_2\text{W}_{20}$; $M = 5921.14$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 14.09300(10)$, $b = 26.7218(3)$, $c = 37.7468(4)$ Å, $V = 14215.1(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.767$ g cm⁻³, $\mu(\text{MoK}\alpha) = 162.26$, $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.054$ for 13768 unique data with $I > 3.0\sigma(I)$ ($R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.077$) and 1068 parameters used for refinement. Crystal data for $[\text{K}(\text{[18]crown-6})]_6\text{H}_2[\mathbf{3}]\cdot 8\text{MeOH}\cdot 4\text{H}_2\text{O}$: $\text{C}_{80}\text{H}_{186}\text{O}_{120}\text{K}_6\text{Si}_2\text{W}_{20}$; $M = 6972.04$, monoclinic, space group $P2_1/n$ (no. 14), $a = 18.547(3)$, $b = 16.564(2)$, $c = 28.633(4)$ Å, $\beta = 99.715(2)^\circ$, $V = 8670.4(21)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.670$ g cm⁻³, $\mu(\text{MoK}\alpha) = 134.80$, $R = 0.047$ for 12297 unique data with $I > 3.0\sigma(I)$ ($R_w = 0.053$) and 598 parameters used for refinement. CCDC 278955 and CCDC 278956 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Baeyer–Villiger oxidation: Catalyst containing 25 μmol of **W** (i.e., **1**: 2.5 μmol, **2** and **3**: 1.25 μmol), solvent (nitromethane, 1.0 mL), H₂O₂ (80% aqueous solution, 0.25 mmol), and substrate (cyclopentanone, 1.25 mmol) were charged to the reaction vial under air. The reaction was carried out at 333 K. The reaction solution was periodically sampled and analyzed by gas chromatography with an internal standard.

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- [13] The platinum diphosphane complex [Pt(μ-OH)(dppb)]²⁺ (dppb = 1,4-bis(diphenylphosphanyl)butane) catalyzes the oxidation of acyclic methyl ketones, but the activity for the oxidation of acetophenone is very low in comparison with those for aliphatic ketones: R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, *Organometallics* **1998**, *17*, 661–667.
- [14] The oxidation of aliphatic and aromatic aldehydes with H₂O₂ mediated by the tungsten peroxo complex [PO₄{W(O)(O₂)₂]₄]³⁻ has been suggested to proceed by a Baeyer–Villiger-type mechanism, although the products are the corresponding carboxylic acids, and formate esters and/or hydrolysis products (i.e., alcohols and phenols) have not been detected: C. Venturullo, M. Gambaro, *J. Org. Chem.* **1991**, *56*, 5924–5931.
- [15] For peracid-mediated Baeyer–Villiger oxidation of 2-methylated cycloalkanones, oxygen insertion between the carbonyl group and the more highly substituted neighboring carbon atom is favorable,^[6] whereas the regioselectivity for (Lewis and Brønsted) acid-catalyzed oxygenation with H₂O₂ is similar to

that observed for **2**: Lewis acid catalyzed systems: a) M. Renz, T. Blasco, A. Corma, V. Fornes, R. Jensen, L. Nemeth, *Chem. Eur. J.* **2002**, *8*, 4708–4717 (δ -methyl- δ -valerolactone: α -methyl- δ -valerolactone = 67:33 with catalysis by $\text{Sc}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_2]_3$); b) K. Mikami, M. N. Islam, M. Yamanaka, Y. Itoh, M. Shinoda, K. Kubo, *Tetrahedron Lett.* **2004**, *45*, 3681–3683 (ϵ -methyl- ϵ -caprolactone: α -methyl- ϵ -caprolactone = 85:15 with catalysis by Sn- β zeolite). The H^+ -mediated (HClO_4) reaction also exhibited a similar selectivity to that with **2** (δ -methyl- δ -valerolactone: α -methyl- δ -valerolactone = 57:43). The chemical shift of the carbonyl carbon atom of DMF (7.5 μmol) in MeNO_2 (0.6 mL) was 163.9 ppm. A downfield shift (4.7–4.8 ppm) was observed on addition of **2** (5 μmol), whereas no shift was observed on addition of **1**. In addition, **2** was much more active for the Mukaiyama aldol condensation. These facts suggest that **2** is more acidic than **1**. The stronger acidity of **2** possibly explains why **2** is more active than **1** for Baeyer–Villiger oxidation.

- [16] Examples of using compounds of early transition metals as catalysts and H_2O_2 as oxidant have been reported. Re catalysts: a) W. A. Herrmann, R. W. Fischer, J. D. G. Correia, *J. Mol. Catal.* **1994**, *94*, 213–223 (cyclobutanone, TON = 13); b) A. M. F. Phillips, C. Romão, *Eur. J. Org. Chem.* **1999**, 1767–1770 (cyclobutanone derivatives, TON = 210–267); c) R. Berinini, A. Coratti, G. Fabrizi, A. Goggiamani, *Tetrahedron Lett.* **2003**, *44*, 8991–8994 (cyclobutanone and 2-adamantanone, TON > 49). Mo catalyst: d) S. E. Jacobson, R. Tang, F. Mares, *J. Chem. Soc. Chem. Commun.* **1978**, 888–889 (cyclopentanone, TON = 12); e) S. Campestrini, F. D. Furia, *J. Mol. Catal.* **1993**, *79*, 13–19 (cyclopentanone, TON = 6).
- [17] Examples of using catalysts based on late transition metals and H_2O_2 as oxidant: Pt catalysts: a) G. Strukul, A. Varagnolo, F. Pinna, *J. Mol. Catal. A* **1997**, *117*, 413–423 (cyclohexanone, TON = 12); b) R. A. Michelin, E. Pizzo, A. Scarso, P. Sgarbossa, G. Strukul, A. Tassan, *Organometallics* **2005**, *24*, 1012–1017 (cyclobutanone, TON = 100); Co catalyst: c) T. Uchida, T. Katsuki, *Tetrahedron Lett.* **2001**, *42*, 6911–6914 (3-(4-chlorophenyl)cyclobutanone, TON = 15).
- [18] Examples of main-group catalysts: a) R. T. Taylor, L. A. Flood, *J. Org. Chem.* **1983**, *48*, 5160–5164 (cyclopentanone, TON = 67); b) G.-J. ten Brink, J.-M. Vis, I. W. C. E. Arends, R. A. Sheldon, *J. Org. Chem.* **2001**, *66*, 2429–2433 (cyclobutanone, TON = 178; cyclopentanone, TON = 178; 2-adamantanone, TON = 198).