

Selective and Shape-Selective Baeyer–Villiger Oxidations of Aromatic Aldehydes and Cyclic Ketones with Sn-Beta Zeolites and H₂O₂

Michael Renz,^[a] Teresa Blasco,^[a] Avelino Corma,^{*,[a]} Vicente Fornés,^[a] Robert Jensen,^[b] and Laszlo Nemeth^[b]

Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

Abstract: Sn-Beta is used as a heterogeneous catalyst for the Baeyer–Villiger reaction with hydrogen peroxide. Cyclic ketones are transformed into the corresponding lactones, while unsaturated ketones are oxidized to the corresponding unsaturated lactones with very high chemoselectivity. The catalyst is also selective for the oxidation of aromatic aldehydes with H₂O₂, producing

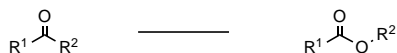
the formate ester or the corresponding hydrolyzed product, that is the alcohol. Shape-selective oxidations are observed for isomeric reactants with different

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molecular shapes. The catalytic Sn sites have been characterized by ¹¹⁹Sn MAS-NMR spectroscopy, and tetrahedral incorporation into the zeolite framework has been demonstrated. In situ IR spectroscopy and ¹⁸O labeling experiments have shown that the oxidation mechanism involves an intermediate of the Criegee type.

Introduction

The Baeyer–Villiger oxidation, which involves the transformation of ketones into esters or lactones [Eq. (1)], is one of the most important reactions in organic chemistry.^[1–3]



The most common and suitable oxidants for this reaction have been peracids, which entail by-products, have a low active oxygen content,^[4] are potentially explosive,^[5] may require strong acidity because of low reactivity.^[1] An additional disadvantage of peracids is their lack of selectivity for oxidation reactions when other functional groups, such as double bonds, are present in the reactant molecule.^[2] To avoid isolation and storage of dangerous peracids, the Mukaiyama method can be employed to generate peracids in situ from corresponding aldehydes,^[6–11] but this process needs a sacri-

ficial organic reactant. The issues encountered with peracids make it desirable to develop catalysts that allow replacement of the peracids by hydrogen peroxide. Some success has been achieved with homogeneous and heterogeneous catalysts containing active centers based on As, Se, Zr, Mo, Re, or Pt, or with soluble and solid acids.^[7, 12–14] All of these catalysts have at least one drawback, such as low activity or selectivity, tedious recovery and regeneration, or high costs for starting materials and/or for safety precautions. Exceptions in this regard among the metal catalysts are soluble Pt complexes, for which turnover numbers (TONs) of 43 and 60 have been reported for cyclohexanone and 2-methylcyclohexanone, respectively, with excellent selectivities to the lactones.^[7] Recently, advances have been reported in the application of peroxyseleninic acids.^[13] With catalytic amounts of the catalyst precursor, cyclopentanone has been converted completely into δ -valerolactone, with a selectivity of 92% in 1,1,1,3,3,3-hexafluoro-2-propanol solvent.^[13] Among the solid acids, sulfonic acid groups fixed to a polymer have been used in the presence of 30% hydrogen peroxide for the Baeyer–Villiger reaction.^[12, 15] The best selectivities achieved with such catalysts were $\approx 80\%$ with cyclopentanone as substrate.^[12] Slightly lower selectivities ($\approx 70\%$) were achieved with acid zeolites and H₂O₂.^[12, 16]

Taking into account the limited success obtained for the Baeyer–Villiger reaction with catalysts that activate H₂O₂, we have very recently reported a different catalytic strategy that involves activation of the carbonyl group instead of the

[a] Prof. Dr. A. Corma, Dr. M. Renz, Dr. T. Blasco, Prof. Dr. V. Fornés
Instituto de Tecnología Química, UPV-CSIC
Universidad Politécnica de Valencia
Avenida de los Naranjos s/n, 46022 Valencia (Spain)
Fax: (+34) 96-3877809
E-mail: acorma@itq.upv.es

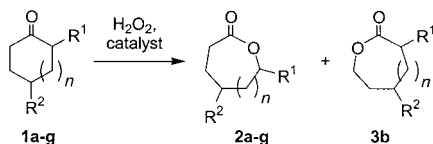
[b] Dr. R. Jensen, Dr. L. Nemeth
UOP LLC, 25 East Algonquin Road
Des Plaines, IL 60017-5017 (USA)

hydrogen peroxide.^[17] Among several Lewis acids, Sn within the framework of a zeolite (Beta) is able to polarize the carbonyl group, making it more reactive towards H_2O_2 attack. If Sn peroxide is formed, it is not active for oxidation reactions^[18] and cannot affect the selectivity negatively when other functional groups are present in the molecule. In the detailed study of the Baeyer–Villiger oxidation with Sn-Beta and H_2O_2 reported here, we have shown that with this catalyst it is also possible to carry out shape-selective Baeyer–Villiger oxidations; we have included the formation of lactones by oxidation of ketones as well as the oxidation of aldehydes to yield the corresponding ester or its hydrolysis products. Additional shape-selectivity effects can occur due to the characteristics of the zeolite support when reacting substrates have different shapes. The study also involved the characterization of the coordination sphere of the active Sn sites by ^{119}Sn MAS-NMR spectroscopy. Mechanistic studies were carried out using in situ IR spectroscopy to elucidate the interaction of the reactant and of the product with the Sn-active sites, and DR-UV spectroscopy to investigate a potential interaction of hydrogen peroxide with the Sn-active sites and with ^{18}O -labeled cyclohexanone to establish the reaction intermediate.

Results and Discussion

Catalytic activity

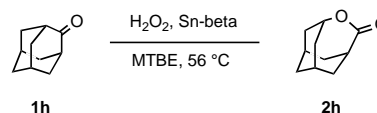
Oxidation of cyclic ketones and shape selectivity effects: The Baeyer–Villiger reaction of cyclohexanone (**1a**) to ϵ -caprolactone (**2a**) was carried out with H_2O_2 as the oxidant, Sn-Beta-2 as the catalyst, and methyl *tert*-butyl ether (MTBE) as the solvent [Eq. (2)].



A TON of 68 was achieved, the lactone being the only product observed (Table 1, entry 1). Increasing the reaction temperature from 56 to 80 °C and use of dioxane as solvent improved the conversion to 52% and the TON to 88 (Table 1, entry 2). We have applied Sn-Beta to another Baeyer–Villiger reaction in which a methyl substituent was introduced in position 2 or 4 of the cyclohexanone ring. A similar activity was found for the two isomers (Table 1, entries 3–6), which indicate that both reactants can diffuse readily into the pores of the zeolite and approach to within reaction distances of the Sn framework. With 2-methylcyclohexanone two regioisomeric lactones were obtained in an 85:15 ratio favoring the insertion of the oxygen between the carbonyl group and the more highly substituted carbon atom neighbor. When conventional peracid oxidants were employed, the minor isomer was observed only in traces (<5%).^[1] Although this behavior of the Sn-Beta system can be regarded as less desirable, it is an

interesting possibility that by modifying this system the selectivity to the uncommon isomer obtained when using peracids could be increased.

To study shape selectivity effects due to the geometrical structure and site accessibility in the zeolite, a *tert*-butyl group was introduced into the cyclohexanone ring instead of the methyl group described above. Whereas 4-*tert*-butylcyclohexanone (**1e**) reacts readily (in dioxane 91% was converted after 3 h; Table 1, entry 9), no conversion was observed with 2-*tert*-butylcyclohexanone (**1d**, entry 7). The very bulky ketone adamantanone (**1h**) has also been oxidized to lactone with excellent conversion and selectivity [Table 1, entries 14 and 15; Eq. (3)].



The lack of conversion in the case of **1d** may have several causes. It has been shown previously that, in general, ketone **1d** can be converted by peracids and the *tert*-butyl group in the 2-position does not prevent the Baeyer–Villiger oxidation.^[19] Consequently, the cause must be related to the interference of the geometries and the sizes of both the substrate molecules and the zeolite pores. The molecular sizes of **1d**, **1e** and **1h** are similar. They have diameters between 6.3 and 7.1 Å (taking the longest distance as the molecular axis) and would fit into the Beta pore of 6.6 Å × 7.7 Å. However, for adamantanone and 4-*tert*-butylcyclohexanone (**1e**) the carbonyl oxygen is part of the molecular axis and therefore far from the apolar zeolite wall. In contrast, for 2-*tert*-butylcyclohexanone (**1d**) the carbonyl oxygen points away from the axis and an unfavorable interaction with the zeolite walls may render diffusion of the molecule within the zeolite pores more difficult. A second explanation for the lack of conversion of **1d** may be that the substituent prevents the approach of the carbonyl group to the metal center, which is embedded in the zeolite wall and shielded by the relatively large oxygen atoms of the zeolite framework.^[20]

Cyclopentanone (**1f**) and 2-methylcyclopentanone (**1g**) could also be oxidized to the corresponding lactones with H_2O_2 using Sn-Beta as catalyst (TONs are nearly 50 and 92, respectively; Table 1, entries 10–13). The oxidant efficiencies were always very high and in no case was decomposition of the hydrogen peroxide observed. Ketones that are less reactive with respect to the Baeyer–Villiger reaction, such as aromatic (acetophenone) and acyclic ketones (3-octanone), are not converted.

Significant advantages of the new oxidation system reported in this work are the heterogeneous nature of the catalyst and the very high selectivity to lactones obtained using H_2O_2 as oxidant. However, from a practical point of view the heterogeneous catalyst should be recyclable. In the case of Sn-Beta, no deactivation of the catalyst was observed after recycling four times without intermediate regeneration steps. This allowed us to obtain a TON higher than 300 without regeneration. Furthermore, Sn-Beta-2 was calcined at 500 °C

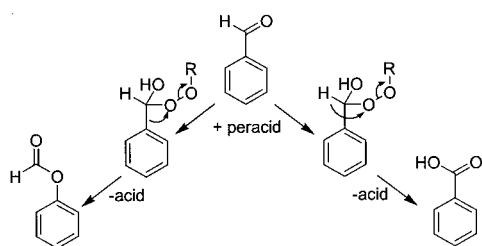
Table 1. Conversions, TONs, and selectivities in the Baeyer–Villiger reaction of various substrates, catalyzed by Sn-Beta-2.

Entry	<i>n</i>	Substrate R ¹ R ²	Reaction conditions	Conversion [%]	TON ^[a]	Selectivity [%] to lactone for H ₂ O ₂
1	1a	1 H H	MTBE, 56 °C, 7 h	42	68	> 98
2			dioxane, 80 °C, 3 h	52	88	> 98
3	1b	1 Me H	MTBE, 56 °C, 7 h	47	86	> 98 ^[b]
4			dioxane, 80 °C, 4 h	80	105	96 ^[b]
5	1c	1 H Me	MTBE, 56 °C, 7 h	46	81	> 98
6			dioxane, 80 °C, 4 h	70	104	97
7	1d	1 <i>t</i> Bu H	MTBE, 56 °C, 7 h	0	0	–
8	1e	1 H <i>t</i> Bu	MTBE, 56 °C, 7 h	54	87	> 98
9			dioxane, 80 °C, 3 h	91	137	> 98
10	1f	0 H H	MTBE, 56 °C, 7 h	32	48	> 98
11			dioxane, 80 °C, 3 h	31	47	> 98
12	1g	0 Me H	MTBE, 56 °C, 7 h	31	47	> 98
13			dioxane, 80 °C, 8 h	62	92	97
14	1h	adamantanone	MTBE, 56 °C, 7 h	85	147	> 98
15	1h	adamantanone	MTBE, 56 °C, 7 h	95 ^[c]	119	> 98

[a] TON, turnover number = catalytic cycles per metal center. [b] An 85:15 mixture of the regioisomeric lactones ϵ -methyl- ϵ -caprolactone and α -methyl- ϵ -caprolactone was observed. [c] 1.1 equiv hydrogen peroxide and 60 mg of Sn-Beta were employed; reaction time 8 h.

in air after the fourth reaction cycle and re-used. The decrease in TON of only 5% can be attributed to the handling of the sample. These results support our conclusion that the Sn-Beta catalyst has very good stability and regenerability which make it suitable for use in a fixed bed or in a stirred continuous reactor.

Oxidation of aromatic aldehydes: The Baeyer–Villiger oxidation of aromatic aldehydes can yield two different products. When the migrating group is the hydrogen atom the corresponding carboxylic acid is formed, but when the aromatic ring migrates the aldehyde is transformed into a formate ester which often becomes hydrolyzed to yield the corresponding phenol (Scheme 1).



Scheme 1. Formation of the ester product (migration of the aromatic ring, left-hand side) and the acid product (migration of the hydrogen atom, right-hand side) in the Baeyer–Villiger oxidation of aromatic aldehydes.

The selectivity to the different products depends on the substituents on the aromatic ring. Electron-donating groups, such as alkoxy, direct the reaction towards ester/phenol formation whereas electron-withdrawing groups favor the formation of the acid. In organic synthesis a phenol is often the desired product, because substituted phenols are important substrates and active compounds in the pharmaceutical industry.^[21]

p-Anisaldehyde (**4a**) and *p*-tolualdehyde (**4b**) could be oxidized by the new oxidation system Sn-Beta/H₂O₂ [Table 2;

Eq. (4)]. With **4a** a mixture of ester and phenol was observed (Table 2, entries 1 and 2), indicating that the aromatic ring is migrating instead of the hydrogen atom. Moreover, the kinetic results (Figure 1) show that the ester is the primary product formed, and it readily reacts to give the phenolic hydrolysis product.

The relative yields of ester and phenol can be modified not only by changing the level of conversion but also by using different solvents. The conversion and selectivity to phenol are higher with toluene than with dioxane as solvent (Table 2).

With the second aldehyde **4b**, migration of both the aromatic ring and the hydrogen atom occurs. As observed with **4a**, conversion is also higher in toluene than in dioxane. However, the solvent has only a minor influence on selectivity to phenol for **4b**.

In summary, phenols with electron-donating substituents can be obtained from the corresponding aldehydes with hydrogen peroxide as oxidant and Sn-Beta as catalyst.

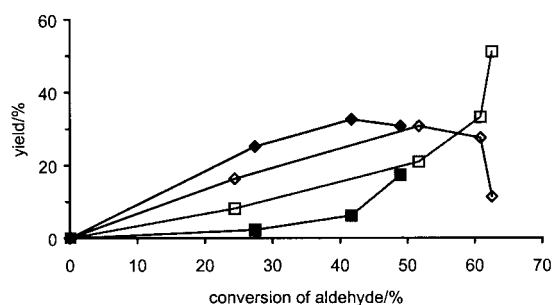


Figure 1. Yield of ester **5a** and alcohol **6a** versus total conversion of aldehyde **4a** in dioxane and toluene as solvents. ♦ yield **5a** in dioxane; ◇ yield **5a** in toluene; ■ **6a** in dioxane; □ **6a** in toluene.

Table 2. Conversions, TONs, and product distributions for the Baeyer–Villiger oxidation of the aromatic aldehydes **4a** and **4b**, catalyzed by Sn-Beta-2.

Entry	Solvent	R	Conversion [%]	TON ^[a]	Product distribution [%]			
					5	6	7	other
1	dioxane	OMe	49	270	63	35	< 2	2
2	toluene	OMe	58	329	13	86	< 2	< 2
3	dioxane	Me	26	166	29	44	23	4
4	toluene	Me	47	300	23	56	20	< 2

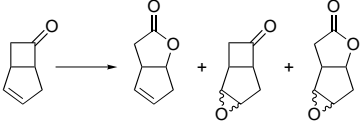
[a] TON, turnover number = catalytic cycles per metal center.

Selection of the appropriate solvent can provide directly a major yield of the desired hydrolysis product, so that an additional saponification step such as the one required when using organic peracids as oxidizing reagents^[22] may not be necessary.

Chemoselectivity of the catalyst for unsaturated ketones: Chemoselectivity towards the lactone product with unsaturated ketones has only been observed with enzymes as catalysts,^[23] or with particular substrates in which the double bond is unreactive and the Baeyer–Villiger reaction is strongly favored. This is because Baeyer–Villiger catalysts such as peracids or methyltrioxorhenium (MTO) are also good epoxidation agents. We have observed chemoselectivity in the Baeyer–Villiger reaction with Sn-Beta catalysts and H₂O₂ [Table 3, Eq. (5)]. When reaction of bicyclohept-3-en-1-one was carried out with *m*-chloroperbenzoic acid (*m*CPBA), a common practice, epoxides were always produced as by-products. In contrast, Sn-Beta yielded exclusively the two regioisomeric lactones. Very similar results have been reported with enzymes as catalysts.^[23] This substrate also furnishes a particular example of enhanced Baeyer–Villiger reactivity of cyclobutanones in the presence of MTO.^[24] Although it is an excellent epoxidation agent, the MTO catalyst provides only the lactone product.^[25]

However, when another reactant, dihydrocarvone, in which both double-bond oxidation and the Baeyer–Villiger oxidation can occur readily, is used to illustrate catalyst chemoselectivity, only Sn-Beta zeolite is fully selective for the lactone [Table 4, Eq. (6)]. The peracid gives a mixture of

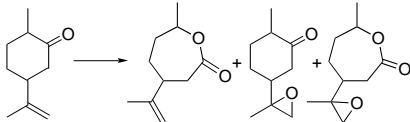
Table 3. Chemoselectivity of the Baeyer–Villiger reaction with various catalysts and H₂O₂.



Catalyst	Product distribution [%]
Sn-Beta	100 ^[a] : 1 : 1
<i>m</i> CPBA	29 : 34 : 37
enzymes	100 ^[a] : 1 : 1
MTO ^[b]	100 ^[c] : 1 : 1

[a] As a 67:33 mixture of regioisomeric lactones; the major isomer is shown. [b] From ref. [25]. [c] Isolated as an 87:13 regioisomeric mixture.

Table 4. Catalyst chemoselectivity in concurrent double-bond oxidation and Baeyer–Villiger oxidation of dihydrocarvone.



Oxidant	Conversion [%]	Product distribution [%]
Sn-Beta/H ₂ O ₂	68	100 : 0 : 0
<i>m</i> CPBA	85	11 : 71 : 18
Ti-Beta/H ₂ O ₂	46	0 : 79 ^[a] : 0
MTO/H ₂ O ₂ ^[b]	9	30 : 33 : 20

[a] The “missing” 21% comprised products from ring-opening of the epoxide. [b] Reaction conditions as in ref. [25].

lactone, epoxide, and epoxylactone, and Ti-Beta produced the epoxide and diols. Under the same reaction conditions MTO lacked reactivity and selectivity, and the lactone was observed only in minor yield.

Characterization and properties of the catalytic sites: To ascertain the coordination of Sn, a ¹¹⁹Sn MAS NMR study was undertaken with a Sn-Beta (1.6 wt % Sn) sample enriched with ¹¹⁹Sn (Sn-Beta-2*). Sn-silicalite (MEL and MFI type) and Sn-MCM-41 have been reported to give ¹¹⁹Sn chemical shifts δ between -670 and -740 ;^[26–30] these spectra were usually recorded on hydrated samples, and the signals were attributed to framework Sn^{IV} sites^[26–30] either in octahedral^[26, 28, 30] or in tetrahedral^[27, 29] coordination. The ¹¹⁹Sn NMR spectrum of dehydrated zeolite Sn-MFI gives a very broad band with the maximum at $\delta = -688$ attributed to octahedral Sn^{IV}, and a shoulder at $\delta = -439$ assigned to framework tetrahedral sites which shifts to $\delta = 579$ when the coordination increases to five upon hydration.^[28] However, the spectra were recorded under static conditions, and therefore the signals were extremely broad (greater than 500 ppm at half height) and the shoulder was ascribed to ill-defined tetrahedral sites.^[28] For the zeolite Sn-Beta-2* after calcination and exposure to air, the ¹¹⁹Sn MAS NMR spectrum of the hydrated sample (Figure 2b) shows two bands at $\delta \approx -690$ and -740 , which are within the chemical shift range typical of Sn^{IV} in hydrated Sn silicalites and Sn-MCM-41 materials.^[26–30] It is important that the spectrum of Sn-Beta zeolite is quite different from that of bulk SnO₂ or SnO₂ impregnated on pure silica-Beta (Figure 2a) or on amorphous SiO₂. For these two materials, only a sharp peak at $\delta = -605$ has been observed, and it is believed to be characteristic of octahedrally coordinated Sn in SnO₂.^[31] Since this peak was not observed in Sn-Beta-2* we can rule out the presence of SnO₂ in this sample, at least at the detection level of NMR. Dramatic changes are observed when zeolite Sn-Beta-2* is dehydrated (Figure 2c). The spectrum consists of a sharp peak at $\delta = -445$, which must originate from tin in a lower coordination state. Under ambient conditions, the original spectrum of the zeolite in the hydrated state is recovered (Figure 2d).

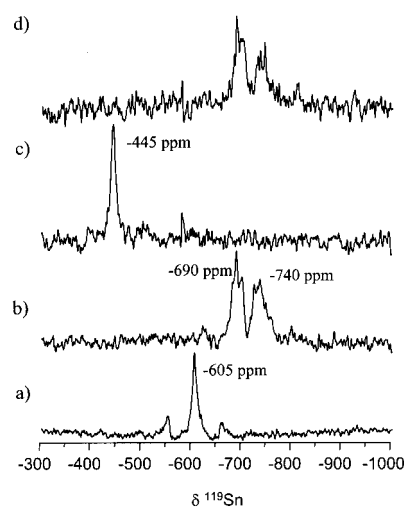


Figure 2. ¹¹⁹Sn MAS NMR spectra of: a) SnO₂-Beta; b) hydrated Sn-Beta; c) dehydrated Sn-Beta; d) rehydrated Sn-Beta.

Accordingly, we attribute the signal at $\delta = -445$ of the dehydrated Sn-Beta-2* zeolite to tetrahedral Sn^{IV} at framework sites, which increases its coordination under ambient conditions by bonding to extra water molecules. The presence of two ^{119}Sn NMR peaks upon hydration could be explained tentatively by the presence of two different coordination states, penta- and hexacoordinated Sn^{IV} . However, considering the position of the low-field peak, we think that hydration induces changes in the local symmetry of the Sn environments leading to two different octahedral sites.

Activity tests with cyclohexanone and Sn-Beta with different tin contents showed that the amount of tin that can be incorporated into network positions is limited. When the Sn content was increased from 0.8 to 1.6 wt % (Table 5; compare entries 1 and 2), conversion increased. When a larger amount of Sn was present (2.36 wt %; entry 3), both conversion and TON decreased. A similar relationship between activity and the amount of metal incorporated into the zeolite framework has been observed previously in the case of Ti-silicalite (TS-1),^[32] where a maximum in activity for alkane or alkene oxidation was found for samples containing $\approx 1.5\%$ Ti. For higher Ti contents, some of the Ti forms Ti–O–Ti pairs and/or is in extra-framework positions, with a deleterious effect on conversion. By analogy, it seems that most of the Sn should be isolated in framework positions and it should be catalytically active for Sn-Beta samples with ≤ 2 wt % Sn. For higher Sn contents, some of Sn must be in extra-framework positions, that is, in SnO_2 crystals. Indeed, we have observed that SnO_2 highly dispersed on silica gel or on pure silica-Beta zeolite gives very little, if any, catalytic activity (Table 5, entries 6 and 7), indicating that the presence of framework Sn is necessary for catalyzing the Baeyer–Villiger reaction with Sn-Beta zeolite.

Furthermore, we have confirmed experimentally that the Sn-zeolite active site remains intact during the reaction and that oxidation does not occur by homogeneous catalysis through leached Sn. Therefore, the reaction was conducted to 30% conversion, the catalyst was filtered out at reaction temperature, and then the reaction was allowed to proceed in the absence of solid catalyst. Under these experimental conditions the reaction did not proceed, and further conversion was not observed after four hours of reaction time. Moreover, in another experiment in which SnCl_4 was used as catalyst the TON was 5, instead of the value of 68 obtained with the Sn-Beta-2 zeolite.

Table 5. Conversions, TONs, and selectivities in the Baeyer–Villiger reaction of cyclohexanone (**1a**), catalyzed by various metal species.

Entry	Catalyst	Conversion [%]	TON ^[a]	Lactone selectivity [%]
1	Sn-Beta-1 (0.8 wt % Sn)	26	87	> 98
2	Sn-Beta-2 (1.6 wt % Sn)	42	68	> 98
3	Sn-Beta-3 (2.3 wt % Sn)	27	30	> 98
4	Ti-Beta (1.2 wt % Ti)	4	4	> 98
5	Al-Beta (0.5 wt % Al)	19	10	> 98
6	$\text{SiO}_2 \cdot \text{SnO}_2$ ^[b]	0	0	
7	Beta $\cdot \text{SnO}_2$ ^[b]	0	0	

[a] TON, turnover number = catalytic cycles per metal center. [b] The same amount of Sn was employed as for the Sn-Beta-2 sample.

Reaction mechanism

Spectroscopic study: To study the role of Sn in the Baeyer–Villiger reaction, we began with two hypotheses: Sn interacts with H_2O_2 to form $\text{Sn}-\text{OOH}$, which attacks the carbonyl group (although organoperoxo complexes of tin(IV) did not exhibit any oxygen transfer reactions);^[18] alternatively, Sn interacts with the carbonyl group, which becomes polarized and consequently can be attacked by the nucleophilic H_2O_2 .

To analyze the first hypothesis, we measured the DR-UV/Vis spectrum of a sample of Sn-Beta treated with H_2O_2 . Contrary to the case of a Ti-Beta sample, where the interaction of Ti with H_2O_2 results in the formation of a band at 425 nm associated with a Ti–OOH species (Figure 3), for Sn-Beta no band in the DR-UV/Vis region was observed. The spectrum was exactly the same for silica-Beta as for pure treated with H_2O_2 (Figure 3).

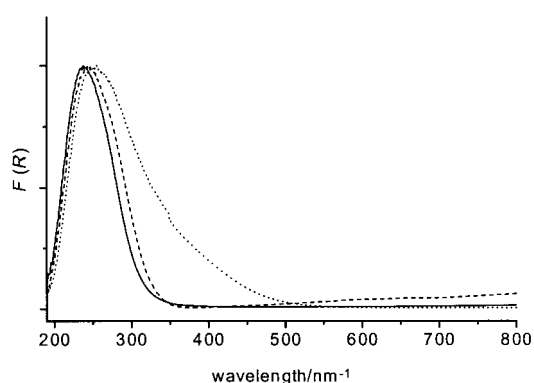


Figure 3. DR-UV/Vis spectra of zeolite samples treated with hydrogen peroxide. (—) Sn-Beta+ H_2O_2 ; (•••) Ti-Beta+ H_2O_2 ; (---) Si-Beta+ H_2O_2 .

Thus, we conclude that even if H_2O_2 can be coordinated to tin in zeolite framework positions, such coordination proceeds without deprotonation and therefore without activation of the H_2O_2 . This conclusion is consistent with the null activity of Sn-Beta for epoxidation of olefins.

The second hypothesis (the interaction of a tin Lewis acid with a carbonyl compound) is well known and documented in the literature. Lewis acid–carbonyl adducts have been observed and investigated by X-ray analysis. Average bond lengths ($d\text{M}-\text{O}$), valence angles ($\alpha\text{C}-\text{O}-\text{M}$), and torsion angles ($\theta\text{X}-\text{C}-\text{M}-\text{O}$) for boron, aluminum, and tin complexes were found by a systematic survey of the Cambridge Structural Database on crystal structures of Lewis acid–carbonyl compound complexes.^[33] In the late 1950s it was discovered that NMR signals and IR bands of carbonyl compounds were shifted upon complexation with a Lewis acid.^[34] In order to explore our second hypothesis—that Sn polarizes the carbonyl group, favoring the H_2O_2 attack—we have made use of these two spectroscopic techniques. Unfortunately, the introduction of molecules into the zeolite structure broadens the NMR signals significantly, and small shifts are difficult to identify. Another limitation was the high dilution of the active sites combined with the corresponding low sensitivity of the analytical method.

However, we determined that IR spectroscopy is an appropriate technique to study the interaction of a ketone (cyclohexanone) with a tin Lewis acid site, on the basis that the carbonyl band in the IR region is very strong and therefore allows the detection of small amounts of adsorbed cyclohexanone.^[35] Therefore, cyclohexanone was adsorbed and then desorbed successively at 50, 100 and 200 °C. Figure 4a shows the IR spectra for Sn-Beta-2. After adsorption at room temperature, an excess of cyclohexanone was physically adsorbed, presenting a typical wavenumber of 1713 cm⁻¹ for the carbonyl band. After desorption at 100 °C, three bands remained: two were in the region of the uncoordinated carbonyl group of cyclohexanone, and one was shifted to 1665 cm⁻¹. The latter was the only band still detected after desorption at 200 °C. This band can be attributed to a tin–oxygen interaction since it does not appear when cyclohexanone is adsorbed/desorbed on a pure silica-Beta zeolite (Figure 4b). With this zeolite, after adsorption of cyclohexanone and after desorption at 50 °C, the band of the normal carbonyl group was obtained. After further desorption at 100 °C, practically all the cyclohexanone was eliminated, and in any case no bands at wavenumbers <1700 cm⁻¹ were

detected. An IR spectrum identical to the one for the pure silica-Beta zeolite was observed when a SnO₂-impregnated silica-Beta sample (1.6 wt % Sn) was subjected to cyclohexanone adsorption/desorption. There is no shift of the IR carbonyl band of cyclohexanone with SnO₂ but it does occur with Sn tetrahedrally coordinated in the framework positions of the zeolite.

When tin is replaced by titanium, a smaller shift of the carbonyl band can be observed. The signal is shifted 32 cm⁻¹ with Ti, compared with 48 cm⁻¹ with Sn (Figure 4c). After desorption at 100 °C only the shifted carbonyl band is detected, and at 200 °C all the cyclohexanone has been desorbed. Both observations, the smaller shift and the easier desorption, suggest that the interaction of the carbonyl oxygen with framework titanium is weaker than the interaction between the carbonyl group and the tin center. This is probably why the activity of Ti-Beta is lower than that of Sn-Beta (see Table 5).

As with the ketone substrate, the lactone produced during reaction can also be coordinated to the Sn center. This is demonstrated when the corresponding series of IR spectra are recorded with ϵ -caprolactone as the adsorbed organic com-

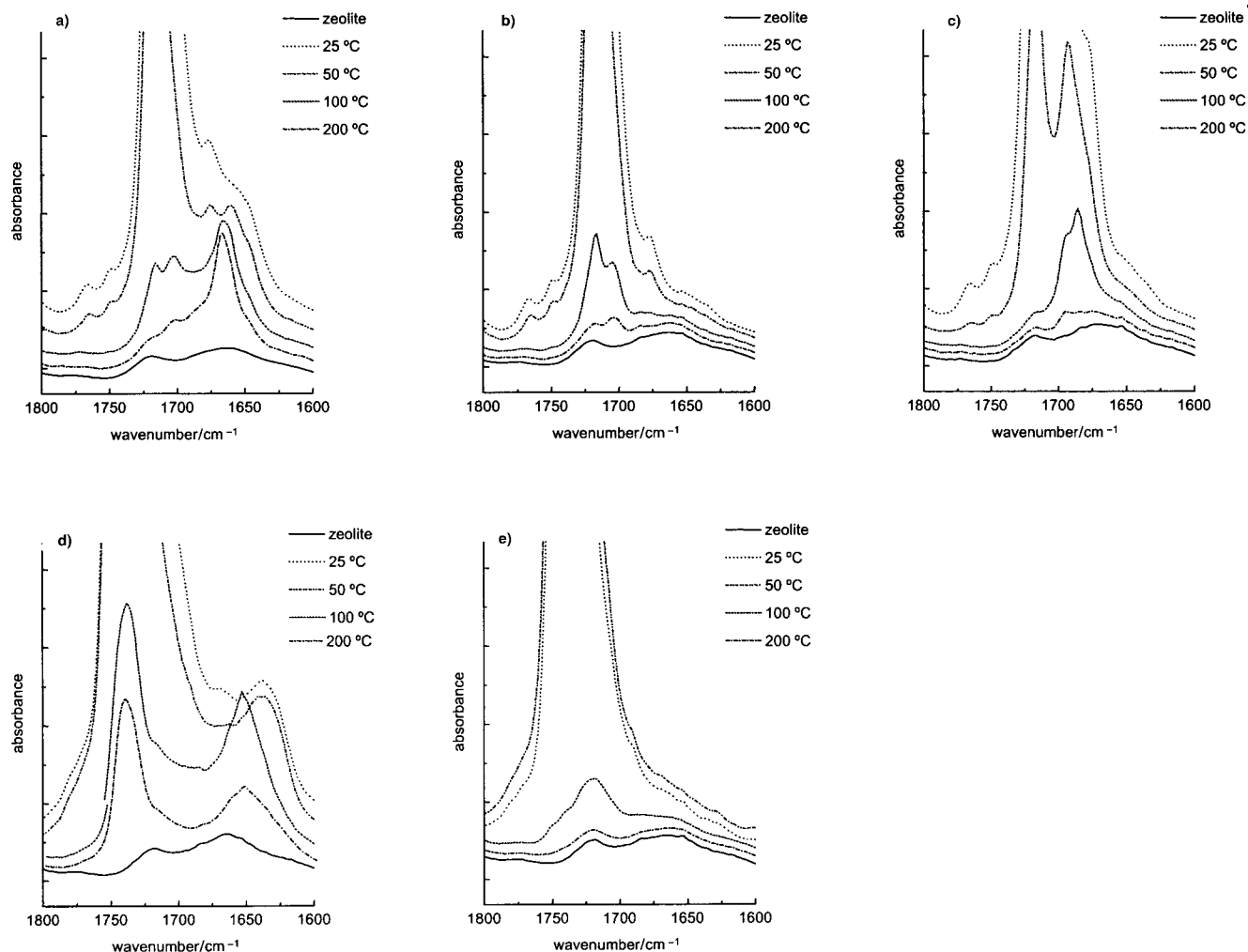
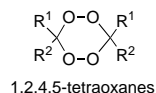


Figure 4. IR spectra of Beta samples before adsorption of cyclohexanone or ϵ -caprolactone (zeolite), after adsorption (25 °C) and after desorption at the corresponding temperature (50 °C, 100 °C, 200 °C): a) cyclohexanone and Sn-Beta; b) cyclohexanone and Si-Beta; c) cyclohexanone and Ti-Beta; d) ϵ -caprolactone and Sn-Beta; e) ϵ -caprolactone and Si-Beta.

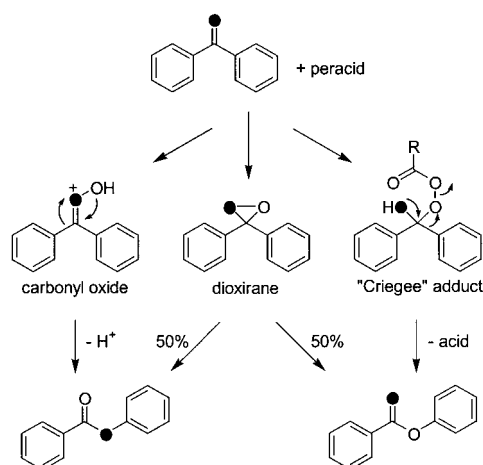
pound and with pure silica-Beta and a Sn-Beta as zeolite samples. With both zeolites the same results are obtained for ϵ -caprolactone and cyclohexanone. In Sn-Beta, the lactone is adsorbed by the metal center, and a shift of the carbonyl band is still present after desorption at 200 °C (Figure 4d). In pure silica-Beta, no shift is observed for the carbonyl band, and the lactone is almost completely desorbed at 100 °C and completely eliminated after desorption at 200 °C (Figure 4e). The coordination of the lactone product indicates that, at high conversions, the substrate competes for coordination to the active center (necessary for activation) with the increasing amount of product.

In summary, it has been shown by IR measurements that the cyclohexanone substrate can coordinate to framework Sn centers, polarizing the carbonyl group and increasing the density of positive charge on the carbon atom of the carbonyl group. This makes the positively charged carbon atom of the carbonyl group more prone to a nucleophilic attack by hydrogen peroxide.

^{18}O labeling experiments: Although the Baeyer–Villiger oxidation was discovered as early as 1899, the mechanism of the reaction was not clarified until 1953.^[1] One potential mechanism, involving 1,2,4,5-tetraoxanes as intermediates, could be excluded since these peroxides were isolated and it was observed that they do not transform into the rearrangement products.^[36]



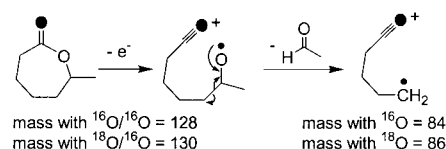
In the 1950s, a dioxirane, a carbonyl oxide, and an adduct of the peracid and a carbonyl group (which was called a Criegee intermediate) were discussed as potential intermediates (Scheme 2).^[37] A benzophenone labeling experiment with ^{18}O proved that the rearrangement could proceed only via the Criegee intermediate.^[38] All labeled oxygen was detected as carbonyl oxygen in benzoic acid phenyl ester, the Baeyer–Villiger product. This result was incompatible with a mechanism involving a dioxirane intermediate because



Scheme 2. Potential mechanism for the Baeyer–Villiger rearrangement with peracids via the carbonyl oxide, the dioxirane, or the “Criegee” intermediate and their consequences for the position of a labeled oxygen atom in the product.

in the latter both oxygen atoms are chemically equivalent, and consequently a statistical 50:50 distribution of carbonyl and alcoholic oxygen would be expected for the labeled products. Also, a carbonyl oxide pathway could be excluded because according to this mechanism all labeled oxygen would be detected as alcoholic, and none as carbonyl.

For the present $\text{H}_2\text{O}_2/\text{Sn-Beta}$ oxidation system, IR measurements showed that the carbonyl group could be activated by coordination to the Lewis acid tin center. It is possible that the oxygen coordinated to the Lewis acid is transformed into a good leaving group after the attack by hydrogen peroxide, and in this way a carbonyl oxide or a dioxirane may be formed. To find out which of these two mechanisms operates in our case, we chose ^{18}O -labeled 2-methylcyclohexanone as reactant. During reaction, it is transformed into the corresponding ϵ -caprolactone, which disintegrates in a mass spectrometer predominantly into two different fragments, each containing one oxygen atom [Eq. (7)].



This outcome makes it feasible to analyze the crude reaction mixture directly by GC-MS without any additional treatment. If the substrate is not 100% labeled, the ratio calculated from mass peaks 128 and 130 gives the labeling content of the whole molecule, which can be compared with the labeling content at the carbonyl position. The latter is obtained from the ratio of mass peaks 84 and 86.

To verify the reliability of the test reaction, the Baeyer–Villiger reaction was first carried out with *m*CPBA. For this oxidant the mechanism is well established and the labeled oxygen should only be detected in the carbonyl position. Indeed, the ratios of the mass peaks 84/86 and 128/130 were identical at 0.11:0.89 [Table 6, Eq. (8)].

Taking the method of preparation of the labeled substrate into account, it was clear that any water molecule (unlabeled) present in the reaction solution would lower the labeling content in the substrate molecule. Consequently, not only was the reaction carried out under anhydrous conditions by using 3 Å molecular sieves to absorb water, but the solvent and *m*CPBA were dried well and stored over 3 Å molecular sieves before use. With these precautions, it was demonstrated that

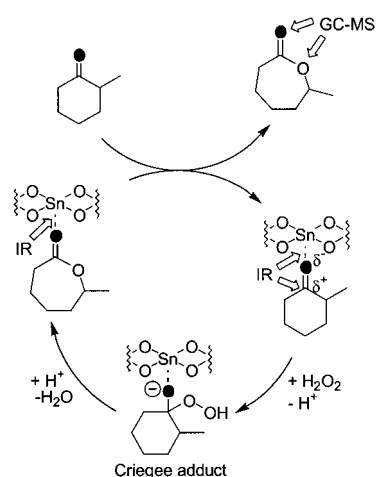
Table 6. Labeled product distribution from Baeyer–Villiger reaction of 2-methyl[^{18}O]cyclohexanone with *m*CPBA.

Reaction conditions	Labeled (^{18}O) content [%]					
	1	2	3	4	5	6
<i>m</i> CPBA, MTBE, 3 Å molecular sieves	89	81	89	0	—[a]	—[a]
Sn-Beta, H_2O_2 , MTBE, MgSO_4 , 30 min	89	57	71	0	0	70

[a] Product not formed with *m*CPBA.

the Baeyer–Villiger reaction with peracids and ^{18}O -labeled 2-methylcyclohexanone was a good test to establish the reaction mechanism.

The oxidation of labeled 2-methylcyclohexanone with hydrogen peroxide catalyzed by Sn-Beta [Eq. (8)] could not be carried out under anhydrous conditions, primarily because water (unlabeled) is always a by-product. Moreover, molecular sieves could not be employed for drying because hydrogen peroxide would be adsorbed as well as water. Therefore, only the solvent was pre-dried with molecular sieves and the reaction was carried out in the presence of MgSO_4 within a short reaction time (30 min). The total amount of labeled oxygen in the lactone product decreased from 89 to 71 %, but the determining observation from a mechanistic viewpoint was that 100 % of the labeled oxygen was found at the carbonyl position. This demonstrates unambiguously that the mechanism of the Baeyer–Villiger oxidation with hydrogen peroxide catalyzed by Sn-Beta proceeds through a Criegee adduct of the hydrogen peroxide with the activated ketone substrate and not through a dioxirane intermediate. Therefore we conclude that the Baeyer–Villiger oxidation of cyclic ketones using H_2O_2 as oxidant and Sn-Beta as catalyst follows the mechanism in Scheme 3.



Scheme 3. Catalytic cycle for the Baeyer–Villiger reaction with hydrogen peroxide, catalyzed by Sn-Beta. First the ketone is coordinated to the Lewis acid center, and thereby the carbonyl group is activated (in situ IR spectroscopy). Then the hydrogen peroxide attacks the more electrophilic carbonyl carbon atom (in situ IR spectroscopy). After the rearrangement step the lactone product is replaced by a new substrate molecule. This mechanism is analogous to that for the peracids and has been proved by an ^{18}O labeling experiment.

The formation of the second product, the regioisomeric α -methyl- ϵ -caprolactone, confirms the conclusions regarding the reaction mechanism, although fragmentation into a species with only a carbonyl oxygen ($-\text{H}_2\text{CO}$ in this case; m/z 98 with ^{16}O and m/z 100 with ^{18}O) was not predominant. The ratio of the 128/130 mass peaks was identical to the ratio for the 98/100 mass peaks, namely 0.30:0.70 and 0.30:0.70, respectively [Eq. (8)]. The reaction mechanism proceeds via the same Criegee intermediate as the main product, but oxygen is inserted into the C–C bond between the carbonyl carbon and its less substituted neighbor.

Conclusion

We have shown that Sn-Beta with Sn tetrahedrally coordinated in zeolite framework positions is an excellent heterogeneous catalyst for Baeyer–Villiger oxidations of cyclic ketones and aromatic aldehydes, with H_2O_2 as oxidant. The system provides excellent catalytic activity and shape selectivity, and also chemoselectivity with unsaturated ketones. Unlike previous catalysts, Sn-Beta activates the carbonyl group but does not activate H_2O_2 . The carbonyl group is then attacked selectively by the H_2O_2 . Labeling experiments with ^{18}O have demonstrated unambiguously that the mechanism of the reaction for the Baeyer–Villiger oxidation with Sn-Beta and H_2O_2 occurs through a Criegee-type intermediate.

Experimental Section

Synthesis of the catalyst: Sn-Beta zeolites with different Sn contents were synthesized according to the following procedure.^[39] Tetraethyl orthosilicate (TEOS) was hydrolyzed in an aqueous solution of tetraethylammonium hydroxide (TEAOH) with stirring. An aqueous solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was then added. In the case of a ^{119}Sn -enriched sample (Sn-Beta-2*), metallic tin enriched with the ^{119}Sn isotope (82.9 %) was dissolved in hydrochloric acid and this solution was used as the source of Sn. The synthesis mixture was stirred until the ethanol formed upon hydrolysis of TEOS had been evaporated. HF was added to the resulting clear solution, and a thick gel was formed with the composition $\text{SiO}_2:x\text{SnO}_2:0.54\text{-TEAOH}:7.5\text{H}_2\text{O}:0.54\text{HF}$. Three gels were prepared with $x=0.0042$, 0.0083, and 0.0125, respectively. They were seeded with nanocrystalline (20 nm crystals) pure silica-Beta at a 1 wt % level. Well crystallized Sn-Beta zeolites with Sn contents of 0.8 (Sn-Beta-1), 1.6 (Sn-Beta-2), and 2.3 wt % (Sn-Beta-3), as determined by chemical analysis, were obtained by crystallization in a rotating Teflon-lined stainless steel autoclave at 140°C for 20 d.

XRD showed the Sn-Beta zeolites calcined at 500°C to be highly crystalline zeolites, and no peaks of SnO_2 were observed in the diffractogram (Figure 5). Nitrogen adsorption experiments on the calcined Sn-Beta samples gave an isotherm very similar to that of pure silica-Beta with micropore volumes of $0.20\text{--}0.21\text{ cm}^3\text{ g}^{-1}$ and BET surface areas of $450\text{--}475\text{ m}^2\text{ g}^{-1}$. The IR spectra in the framework vibration regions of Sn-Beta-1 and pure silica-Beta are shown in Figure 6.

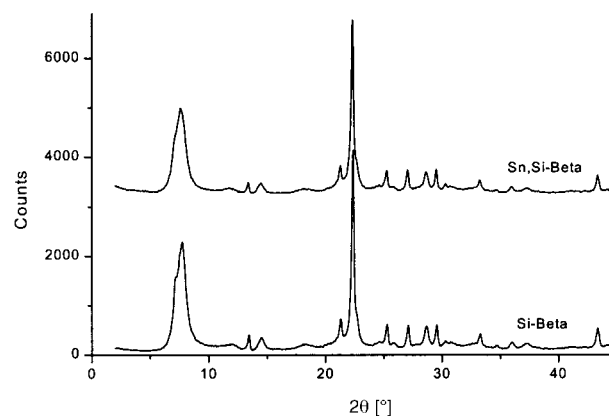


Figure 5. X-ray diffraction patterns of calcined Sn-Beta and pure silica-Beta zeolites.

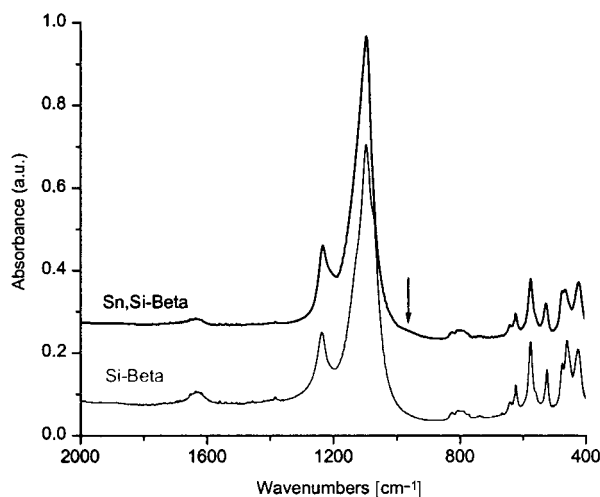


Figure 6. IR spectra in the framework vibration region of calcined Sn-Beta and pure silica-Beta zeolites.

The spectra of the two samples are very similar except for a shoulder at $\approx 960\text{ cm}^{-1}$ exhibited by the Sn-containing Beta. This band has also been observed in other zeolites containing framework metals and has been attributed to Si–O–M vibrations.^[26] Although its origin is still under discussion, it is generally taken as an indication of metal incorporation into the framework.

^{119}Sn MAS NMR spectra: These were recorded with a Varian VXR-S400 WB spectrometer at a frequency of 149.0 MHz using a 5 mm high-speed dot probe. Samples were packed into silicon nitride rotors and spun at 8 kHz. The spectra were recorded using pulses of 3.5 μs to flip the magnetization at 60° with recycle delays of 50 s. Chemical shifts are referred to tetramethyltin using SnO_2 as a secondary reference ($\delta = -604$). For measurements with dehydrated samples, the zeolites were treated under dynamic vacuum at 400°C overnight and transferred to the rotor within a glovebox under an atmosphere of nitrogen. The spectrum of rehydrated samples were acquired after exposing the “dehydrated samples” to ambient conditions for several hours.

In situ IR measurements: For the IR study of the interaction of cyclohexanone with Sn-Beta and other zeolites, the solid was first treated overnight at 400°C under dynamic vacuum (10^{-4} Torr) to remove adsorbed H_2O , then cyclohexanone was adsorbed and the IR spectrum was recorded. Afterwards, the ketone was desorbed successively at 50, 100, and 200°C . An IR spectrum was recorded after each desorption.

Oxidations: Ketones and solvents of the highest purity available ($\geq 98\%$) were purchased from Aldrich and used without further purification. The only exceptions were bicyclo[3.2.0]hept-2-en-6-one (Merck; purity $> 95\%$) and hydrogen peroxide (Fluka; 35 wt% in water). GC analyses were carried out on an HP 5890 gas chromatograph equipped with a 25 m HP-5 column and an adequate temperature programming capability. A Fisons 8035 gas chromatograph coupled with a Fisons MD 800 mass spectrometer was used for GC-MS analyses to identify products. The labeling experiments were analyzed by GC-MS on an Agilent HP 6890 apparatus.

General procedure for the Baeyer–Villiger oxidation with H_2O_2 and Sn-Beta: The ketone ($\approx 1\text{ mmol}$) and hydrogen peroxide (35% H_2O_2 ; $\approx 1.5\text{ mmol}$) were dissolved in MTBE (3.00 g), or the ketone ($\approx 1\text{ mmol}$) and hydrogen peroxide (35% H_2O_2 ; $\approx 3\text{ mmol}$) were dissolved in dioxane (3.00 g). A sample (50 mg) of the catalyst was added, and the reaction mixture was stirred and heated to 56°C (MTBE) or 80°C (dioxane) for 7 h. The reaction was followed by gas chromatography, and the products were identified by comparison with reference samples by GC-MS spectroscopy, or after purification by ^1H NMR spectroscopy. In the case of the aromatic aldehydes, the aldehyde (3.7 mmol) and hydrogen peroxide (35%; 5.1 mmol) were dissolved in dioxane (3.0 g) or toluene (3.0 g). A sample (50 mg) of catalyst Sn-Beta-2 was added, and the reaction mixture was stirred and heated to 80°C for 7 h.

Preparation of ^{18}O -labeled 2-methylcyclohexanone: 2-Methylcyclohexanone (500 mg, 4.46 mmol) and H_2^{18}O ($\approx 96\%$ ^{18}O ; 1.00 g, 49.8 mmol) were stirred in a biphasic system at room temperature. The reaction was followed

by GC-MS; after 2 h the theoretical maximum ^{18}O content of 89.1% was reached. The resultant ketone was used without any further treatment or purification. MS: m/z (%): 114 (83.4) $[M]^+$, 112 (9.29), 68 (100).

Preparation of a solution of H_2O_2 in MTBE: An aqueous H_2O_2 solution (35% H_2O_2 ; 5 mL; 4.52 g) was stirred with MTBE (20 mL; 18.4 g). MgSO_4 was added to remove the water. After decantation, the drying process was repeated, and the MgSO_4 was removed by filtration. The H_2O_2 content of the resultant sample was $7.1 \pm 0.6\%$.

Preparation of a solution of *m*CPBA in MTBE: *m*CPBA (500 mg) was dissolved in MTBE (5 mL; 3.70 g). The solution was dried with MgSO_4 and the final content of *m*CPBA was 9.7%. For the reaction under anhydrous conditions, this solution was dried with molecular sieves.

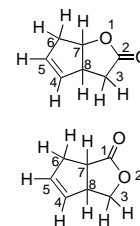
Oxidation of 2-methyl[^{16}O]cyclohexanone (unlabeled) with H_2O_2 catalyzed by Sn-Beta-2: 2-Methylcyclohexanone (48 mg; 0.428 mmol) was added to a mixture of an H_2O_2 solution (7.1% H_2O_2 ; 139 mg; 0.291 mmol) in MTBE, and MTBE (1.50 g) and the reaction was started with the addition of Sn-Beta-2 (25 mg). The reaction mixture was heated to 56°C for 3 h. The solids were removed and the solution was submitted directly to GC and GC-MS analysis. Conversion 44%; products ϵ -methyl- ϵ -caprolactone and α -methyl- ϵ -caprolactone (83:17 mixture). Unconverted 2-methylcyclohexanone: MS m/z (%): 114 (0.472), 112 (91.7) $[M]^+$, 110 (1.08×10^{-3}), 68 (100). α -Methyl- ϵ -caprolactone: MS m/z (%): 130 (0.0232), 128 (1.37) $[M]^+$, 126 (2.67×10^{-3}), 86 (2.03), 84 (78.5), 82 (0.280), 55 (100). ϵ -Methyl- ϵ -caprolactone: MS m/z (%): 130 (0.0206), 128 (28.5) $[M]^+$, 126 (9.69×10^{-3}), 100 (0.644), 98 (15.6), 96 (0.0398), 56 (95.9), 55 (100).

Oxidation of 2-methyl[^{18}O]cyclohexanone with *m*CPBA in the presence of 3 Å molecular sieves: 2-Methyl[^{18}O]cyclohexanone (53 mg; 0.464 mmol) was added to *m*CPBA solution (9.67% *m*CPBA; 506 mg; 0.283 mmol) in MTBE (dried over 3 Å molecular sieves), anhydrous MTBE (1.00 g), and 3 Å molecular sieves, and the reaction mixture was heated to 56°C for 1 h. The solids were removed by filtration and the solution was submitted directly to GC and GC-MS analysis. Conversion 14%; ϵ -methyl- ϵ -caprolactone was the exclusive product. Unconverted 2-methyl[^{18}O]cyclohexanone: MS m/z (%): 114 (73.8) $[M]^+$, 112 (17.8), 68 (100); ^{18}O content 80.5%; ϵ -methyl- ϵ -caprolactone: MS m/z (%): 130 (1.26) $[M]^+$, 128 (0.155), 86 (90.6), 84 (11.4), 57 (100). ^{18}O content in the molecule 89.2%; ^{18}O content in carbonyl position 89.1%.

Oxidation of 2-methyl[^{18}O]cyclohexanone with H_2O_2 catalyzed by Sn-Beta: 59 mg (0.517 mmol) of 2-methyl[^{18}O]cyclohexanone was added to the mixture of an H_2O_2 solution (7.1%; 113 mg; 0.236 mmol) in MTBE, anhydrous MTBE (1.63 g) and MgSO_4 (39 mg). The reaction was started with the addition of Sn-Beta-2 (25 mg). The reaction mixture was heated to 56°C for 30 min. To stop the reaction, by removing the water and the unconverted H_2O_2 , molecular sieves (3 Å) were added. After 1 h, the solids were removed by filtration and the solution was analyzed directly by GC and GC-MS. Conversion 20%; the product was an 85:15 mixture of ϵ -methyl- ϵ -caprolactone and α -methyl- ϵ -caprolactone. Unconverted 2-methyl[^{18}O]cyclohexanone: MS m/z (%): 114 (51.4) $[M]^+$, 112 (38.6), 68 (100); ^{18}O content 57.0%. ϵ -Methyl- ϵ -caprolactone: MS m/z (%): 130 (1.13) $[M]^+$, 128 (0.485), 86 (86.8), 84 (34.4), 57 (100). ^{18}O content in the molecule 70.0%; ^{18}O content in carbonyl position 71.6%. α -Methyl- ϵ -caprolactone: MS m/z (%): 130 (19.7) $[M]^+$, 128 (8.53), 100 (11.5), 98 (4.80), 56 (100), 55 (99.6). ^{18}O content in the molecule 69.8%; ^{18}O content in carbonyl position 70.2%.

Determination of the configuration of the regioisomers in the oxidation of bicyclohept-3-en-1-one by ^1H NMR spectroscopy: Major isomer, 1-oxabicyclooct-4-en-2-one:^[40] ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 2.48$ (dd, $J = 0.8, 18\text{ Hz}$, 1H), 2.75 (m, 3H), 3.53 (m, 1H), 5.15 (ddd, $J = 2.4, 3.9, 6\text{ Hz}$, 1H, 7-H), 5.60 (m, 1H, 4-H or 5-H), 5.80 (m, 1H, 4-H or 5-H).

Minor isomer, 2-oxabicyclooct-4-en-1-one: ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 2.75$ (m, 3H), 3.15 (dt, $J = 2.7, 7.5\text{ Hz}$, 1H), 3.60 (m, 1H), 4.25 (dd, $J = 1.5, 9.3\text{ Hz}$, 1H, 3-H), 4.44 (dd, $J = 7.0, 9.3\text{ Hz}$, 1H, 3-H), 5.66 (m, 1H, 4-H or 5-H), 5.88 (m, 1H, 4-H or 5-H).



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