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Regioselective Cleavage of Electron-Rich Double Bonds in Dienes to Carbonyl Compounds with [Fe(OTf)$_2$(mix-BPBP)] and a Combination of H_2O_2 and $NaIO_4$

CLUSTER ISSUE

Peter Spannring,[a] Vital A. Yazerski,[a] Jianming Chen,[a]
Matthias Otte,[a] Bert M. Weckhuysen,[b] Pieter C. A. Bruijnincx,[b]
and Robertus J. M. Klein Gebbink*[a]

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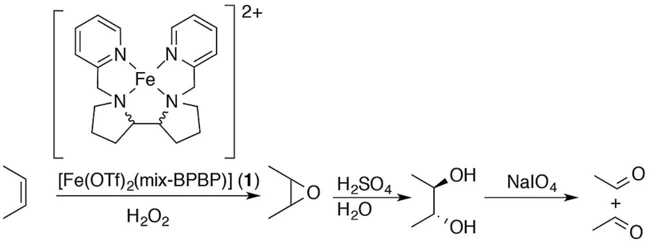
A method for the regioselective transformation of dienes to carbonyl compounds has been developed. Electron-rich olefins react selectively to yield valuable aldehydes and ketones. The method is based on the catalyst [Fe(OTf)$_2$(mix-BPBP)] with an oxidant combination of H_2O_2 (1.0 equiv.) and $NaIO_4$ (1.5 equiv.); it uses mild conditions and short reaction times, and it outperforms other olefin cleavage methodologies.

Introduction

The oxidative cleavage of alkenes into aldehydes is a reaction of both commercial and synthetic interest, an example being the transformation of renewable feedstock, including fatty acids, into valuable products.[1–3] Indeed, ozonolysis is performed on an industrial scale on a series of alkenes,[4] including oleic acid. The use of ozone comes with significant disadvantages, however, as a result of the explosion risks associated with its use.[1] Catalytic oxidative cleavage methods using more benign oxidants are typically limited to second- and third-row transition metal complexes, such as the Ru/$NaIO_4$,[5,6] Os/$NaIO_4$[7] and W/H_2O_2-based[8] combinations that have been applied to a variety of alkenes.[9] Catalysts based on first-row transition metals, in particular those based on Fe, would be desirable for oxidative cleavage reactions, as such systems are likely to be cheaper, less toxic, and more sustainable.[10–17] Examples of such catalyst systems are very scarce, the reported examples predominantly being applied to styrene-type substrates[10–17] rather than to more challenging substrates that contain nonactivated internal, aliphatic double bonds. It is the latter type of olefins that are found in renewable substrates such as unsaturated fatty acids and terpenes.

We have previously reported the first example of an Fe-based one-pot oxidative cleavage of a number of alkenes and unsaturated fatty acids into aldehydes.[18] This oxidative cleavage method involves sequential [Fe(OTf)$_2$(mix-BPBP)]-catalyzed alkene epoxidation with H_2O_2 [mix-BPBP is a mixture of *R*,*S*-, *R*,*R*-, and *S*,*S*-isomers of *N*,*N′*-bis(2-picolyl)-2,2′-bipyrrolidine],[19–22] followed by H_2SO_4-induced hydrolysis of the epoxide to the diol, and finally cleavage of the latter species to the aldehydes by $NaIO_4$ (Scheme 1). This method can be run at a low catalyst loading (0.5 mol-%) and uses H_2O_2 (1.5 equiv.) as one of the terminal oxidants in combination with a stoichiometric amount of $NaIO_4$ (1.0 equiv.) at ambient temperatures without over-oxidation to the carboxylic acids.



Scheme 1. Oxidative cleavage protocol for electron-rich alkenes and unsaturated fatty acids with [Fe(OTf)$_2$(mix-BPBP)].[18]

Oxidative cleavage methods, such as those using ozone, Ru- or Os-based catalysts, as well as our previously reported non-metal-mediated cleavage with oxone/$NaIO_4$,[23] can oxidize a wide variety of alkenes. As a result, a common downside of these protocols is the lack of regioselectivity in the oxidation of substrates that contain more than one C=C double bond, as all double bonds in such polyenes typically get oxidized with these systems. For synthetic purposes, it

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[a] Organic Chemistry & Catalysis,
Debye Institute for Nanomaterials Science,
Universiteit Utrecht,
Universiteitsweg 99, 3584 CG, Utrecht, The Netherlands
E-mail: r.j.m.kleingebbink@uu.nl
http://www.uu.nl/en/research/organic-chemistry-catalysis
[b] Inorganic Chemistry & Catalysis,
Debye Institute for Nanomaterials Science,
Universiteit Utrecht,
Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

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is useful to be able to selectively cleave one double bond and leave others untouched, in order to arrive at dicarbonyl-functionalized alkenes. Although challenging, the ability to synthesize such dicarbonyl compounds is rewarding, as these are interesting chemical building blocks, for example for the synthesis of unsaturated primary diamines.[24]

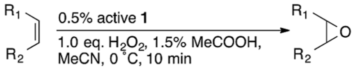
Examples of such regioselective cleavage methods are very limited. The selective oxidative cleavage of only one double bond in a diene has, for instance, been reported with [Mn{TPP-(PEO$_{750}$)$_4$}]Cl [TPP-(PEO$_{750}$)$_4$ = 5,10,15,20-tetrakis(4-PEO$_{750}$-phenyl)porphyrin; PEO = polyethylene glycol], 3.0 equiv. $NaIO_4$ and 1.0 equiv. of imidazole, converting limonene to give 6-oxo-3-isopropyleneheptanal in 89 % yield after 24 h.[16] No other examples of regioselective diene cleavage were reported for this system, however. To the best of our knowledge, the only report that specifically focuses on regioselective cleavage of one double bond in dienes uses [*cis*-Ru(dmp)$_2$(H_2O)$_2$](PF_6)$_2$[25] (dmp = 2,9-dimethylphenanthroline) with H_2O_2. Only the more accessible double bonds of the dienes are cleaved into aldehydes with this system, showing that regioselectivity is based on steric factors.[26] With this system, 1 mol-% catalyst loading and an excess of H_2O_2 (10 equiv.) are used to cleave the terminal double bonds in limonene and 4-vinyl-1-cyclohexene, but only in 11–21 % yield after 6 h at 50 °C. The results obtained with geraniol, which is converted into geranial, show that alcohol functional groups are not tolerated by this system, with oxidation of the alcohol to the aldehyde being preferred over alkene cleavage.

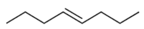
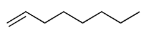
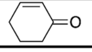
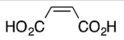
Here, we report that a combination of [Fe(OTf)$_2$(mix-BPBP)] (**1**) and H_2O_2/H_2SO_4/$NaIO_4$[18] can regioselectively form alkenedicarbonyl compounds by selective cleavage of the electron-rich C=C bond in various dienes, showing that the selectivity of the reaction is based on electronic factors, regardless of the accessibility of the double bond.

Results and Discussion

The epoxidation step is the regioselectivity-inducing step of the overall cleavage protocol, which comprises subsequent epoxidation, epoxide hydrolysis, and finally diol cleavage; this reaction was thus first studied with a series of aliphatic alkenes in the presence of **1**.[27] In an epoxidation protocol dubbed method A, 1.0 equiv. of substrate, 0.5 mol-% active catalyst, 1.5 mol-% MeCOOH,[27–29] and 1.0 equiv. of H_2O_2 were reacted in the presence of **1** at 0 °C for 10 min. A range of aliphatic alkenes, involving *cis*-, *trans*-, tri-, and tetra-substituted alkenes as well as longer-chain alkenes could all be epoxidized in high yields (Table S1). This is exemplified by the epoxidation of *cis*-4-octene, which was nearly quantitatively converted into the epoxide (Table 1, entry 1). The slightly lower conversion of *trans*-4-octene (Table 1, entry 2) indicated negligible differences in reactivity between *cis*- and *trans*-alkenes. Conversion decreased more significantly to 85 % for 1-octene (Table 1, entry 3) and to 60 % for 2-cyclohexen-1-one (Table 1, entry 4), indicating lower reactivities for terminal and electron-poor alkenes. This is further illustrated by the low conversion obtained in the reaction of maleic acid (Table 1, entry 5) as well as other electron-deficient substrates. Indeed, epoxide yields dropped systematically with decreasing electron density on the C=C double bond (Table S2). The selectivity for the epoxide was high for all substrates, though.

Table 1. Epoxidation of monoenes.[a]

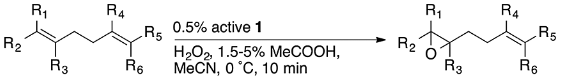


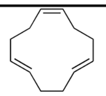
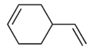
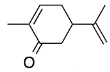
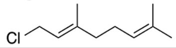
Entry	Substrate	Conversion (%)	Epoxide (%)
1		98	97
2		94	94
3		85	85
4		60	55
5		15	15

[a] Reaction conditions: Method A: 0.5 mol-% of the sum of [Fe(OTf)$_2$(*R*,*R*-BPBP)] and [Fe(OTf)$_2$(*S*,*S*-BPBP)] (**1**), 1 equiv. H_2O_2, 1.5 mol-% MeCOOH, MeCN, 0 °C, 10 min, yields determined by NMR spectroscopy.

The results above show the potential of the method for regioselective epoxidation, which was further explored for some polyenes, but now with a limited amount of H_2O_2 to prevent over-epoxidation (Tables 2 and S3).[27,30] With 1,5-cyclooctadiene, the monoepoxide 1,2-epoxy-*cis*-5-cyclooctene can be obtained in high yield (Table S3). The reaction with 1,5,9-*cis*-*trans*-*trans*-cyclododecatriene, a polyene with distinct double bonds, and 0.6 equiv. H_2O_2 resulted in a monoepoxide mixture, with a *trans*-epoxide/*cis*-epoxide ratio of 2:1 in 51 % yield based on the substrate (Table 2, entry 1). The oxidation of 4-vinyl-1-cyclohexene with 0.9 equiv. H_2O_2 showed excellent selectivity towards the internal

Table 2. Regioselective epoxidation of polyenes.[a],[27]



Entry	Substrate	H_2O_2 (eq.)	Mono-epoxide (%)	Endo/*trans* (%)	Exo/*cis* (%)
1		0.6	51	34	17
2		0.9	79	74	5
3[b]		1.0	98	-	98
4[c]		1.0	65	-	-

[a] Reaction conditions: Method A, 5 mol-% MeCOOH, isolated monoepoxide yields. [b] 1.5 mol-% MeCOOH. GC yield, 99 % conversion. [c] 1.5 mol-% MeCOOH, yield determined by NMR spectroscopy.

double bond, with a 74% yield of the endocyclic epoxide formed at 79% combined monoepoxide yield (Table 2, entry 2). The exocyclic monoepoxide of carvone could even be obtained in 98% yield with 1.0 equiv. H_2O_2 (Table 2, entry 3). Optimization of the conditions for the oxidation of carvone resulted in quantitative conversion and furthermore showed that a limited amount of oxidant and short reaction times are crucial to prevent over-epoxidation (Table S4). Geranyl chloride proved to be a suitable substrate as well. Here, oxidation occurs selectively at the C=C double bond remote from chloride with 65% yield (Table 2, entry 4). Notably, such epoxyolefins are valuable substrates for radical-type 5-*exo*-cyclizations.[31]

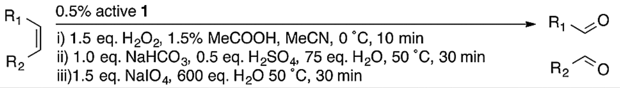
Overall, the intrinsic differences in reactivity between the monoenes are clearly reflected in these reactions. A previously reported protocol for the regioselective epoxidation of electron-rich alkenes involved 4–8 mol-% of a polymer-supported Mn catalyst, 43 mol-% imidazole, and 2 equiv. $NaIO_4$ with reaction times of 24–42 h.[30] The conditions presented here as part of the overall oxidative cleavage protocol thus constitute an attractive alternative for regioselective epoxidation of electron-rich olefins.

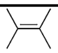
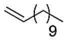
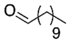
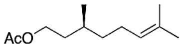
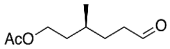
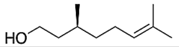
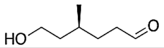
Having established that regioselectivity can be induced in the epoxidation step, the reaction conditions were optimized for full oxidative substrate cleavage. The one-pot oxidative cleavage protocol thus involved substrate epoxidation at 0 °C for 10 min with **1** (0.5 mol-%), H_2O_2 (1.5 equiv.), and MeCOOH (1.5 mol-%), followed by an increase of the reaction temperature to 50 °C and epoxide hydrolysis with H_2SO_4 [0.5 equiv. in H_2O (75 equiv.)] for 30 min to yield the diol. Finally, 1.0 equiv. $NaHCO_3$ was introduced at 50 °C to neutralize the reaction mixture, followed by treatment for 30 min with $NaIO_4$ (1.0 equiv. in H_2O; method B, see Supporting Information for details).

A variety of aliphatic alkenes, including di-, tri-, and tetrasubstituted aliphatic alkenes, could be cleaved with this method in high yield (Table S5). Highlighted examples are the near-quantitative cleavage of tetramethylethylene to acetone (Table 3, entry 1) and the formation of undecanal with high selectivity at near-quantitative conversion of 1-dodecene (Table 3, entry 2). Furthermore, the protocol allowed the chemoselective oxidative cleavage of citronellol and citronellol acetate with high isolated yields of the aldehydes at full substrate conversion (Table 3 entries 3 and 4), showing that acetate and alcohol groups are tolerated by this procedure.

Subsequently, the oxidative cleavage of dienes was investigated with only 1.0 equiv. of H_2O_2 to limit potential overepoxidation (Table 4). Reactions with 1,3-cyclohexadiene and 1,5-cyclooctadiene gave 49% and 67% isolated yields of the corresponding alkenedials, respectively (Table 4, entries 1 and 2). Motivated by these results we studied the regioselective oxidative cleavage of nonsymmetric dienes (Table 4, entries 3–7). The reaction of 4-vinylcyclohexene showed that the internal double bond is preferentially cleaved, yielding 76% of 3-vinyl-adipaldehyde at 92% conversion (Table 4, entry 3). Oxidative cleavage of geraniol resulted in 54% of *trans*-6-hydroxy-4-methyl-4-hexen-1-one at 70% conversion, also indicating that the allylic alcohol remained predominantly untouched, forming only trace amounts of 4-oxo-1-pentanone (Table 4, entry 4). The influence of the difference in olefin electron density on regioselective cleavage can be clearly seen from the reactions with 4-vinylcyclohexane, geraniol, and carvone. While the reactions with the first two substrates show good, but not complete, regioselectivities of approximately 80%, the oxidative cleavage of carvone is completely regioselective. Only the exocyclic double bond in carvone is cleaved, even with 1.1 equiv. H_2O_2 (Table 4, entry 5). Carboxylic acids and sec-

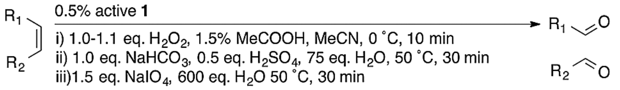
Table 3. Chemoselective oxidative cleavage of monoenes.[a]

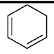
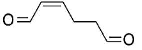
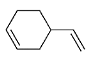
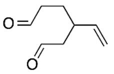
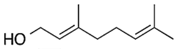
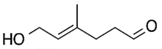
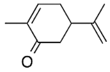
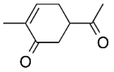
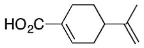
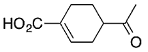
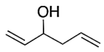
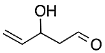


Entry	Substrate	Conv. (%)	Product	Yield (%)
1		100		94
2		92		85
3		100		80[b]
4		100		68[b,c]

[a] Method B: i) 0.5% active **1**, 10 min, 0.015 equiv. MeCOOH, 1.5 equiv. H_2O_2, 0 °C in MeCN, ii) 0.5 equiv. H_2SO_4 in 75 equiv. H_2O, 50 °C, 0.5 h, iii) 1 equiv. $NaHCO_3$, 1.5 equiv. $NaIO_4$ and 600 equiv. H_2O at 50 °C, 0.5 h, yield determined by NMR spectroscopy. [b] Isolated yield. [c] 1 equiv. MeCOOH, traces of cyclization product.

Table 4. Oxidative cleavage of dienes.[a]



Entry	Substrate	Conv. (%)	Product	Yield (%)
1		66		49[b]
2		88		67
3		92		76[c]
4		70		54[d]
5		100		99[e]
6[f]		82		59
7		55		43[c]

[a] Reaction conditions: Method B, but with 1.0 equiv. H_2O_2, isolated yield. [b] Traces of 1,4-butanedial observed. [c] Yield determined by NMR spectroscopy. [d] Yield determined by NMR spectroscopy, trace amounts of 4-oxo-1-pentanone. [e] 1.1 equiv. H_2O_2 added, GC yield. [f] 1.0% active **1** used.

ondary allyl alcohols are also tolerated under our reaction conditions (Table 4, entries 6 and 7): perillic acid is preferentially cleaved at the exocyclic double bond, yielding 59% of the corresponding ketone at 82% conversion. The secondary alcohol 1,5-hexadien-3-ol is transformed selectively into 3-hydroxy-pent-4-enal (43% at 55% conversion). Unfortunately, apart from the successful conversion of 1,3-cyclohexadiene, other conjugated dienes or trienes gave only little or no identified aldehyde product.

Conclusions

A regioselective Fe-based oxidative cleavage protocol was developed for the conversion of electron-rich internal and terminal olefins to the corresponding carbonyl compounds with low oxidant loadings and short reaction times. The protocol shows a unique electronic preference for the cleavage of electron-rich alkenes over less electron-rich alkenes and for internal alkenes over external alkenes. The observed selectivity is based on electronic rather than steric factors, as also less accessible electron-rich double bonds are cleaved. The selective oxidation of geraniol, perillic acid, and 1,5-hexadien-3-ol furthermore shows the functional group tolerance of the protocol. The low catalyst loading, short reaction time, and functional group tolerance of the system compare favorably with other regioselective systems.[16,26] The system is the first regioselective cleavage system of internal double bonds reported for multiple types of dienes. The method also outperforms protocols using Ru, Os, and W oxides in the sense that these generally cannot discriminate between the double bonds in polyenes or overoxidize the initial aldehyde product to the carboxylic acid level.[23,32,33] Overall, this Fe-based cleavage protocol provides a practical and mild procedure that allows for the (regio)selective formation of aldehydes and ketones, without significant over-oxidation.

Experimental Section

Monoalkene Epoxidation, Method A: Alkene substrate (0.72 mmol), active [Fe(OTf)$_2$(mix-BPBP)] (**1**) {0.5%; containing 3.6 µmol of combined [Fe(OTf)$_2$(*S*,*S*-BPBP)] and [Fe(OTf)$_2$(*R*,*R*-BPBP)], in a batch commonly containing inactive [Fe(OTf)$_2$(*R*,*S*-BPBP)] (0.9–1.2 µmol)},[27] MeCOOH (0.015 equiv.), and MeCN (3 mL) were mixed at 0 °C. H_2O_2 (1.0 equiv.) in MeCN (0.5 mL) was added dropwise by hand, and the mixture was stirred for 10 min prior to addition of diethyl ether (20 mL) and nitrobenzene (1.0 equiv., internal standard) in MeCN (1 mL), and subjected to GC analysis to determine the conversion for *cis*-4-octene, *trans*-4-octene, 1-decene, 2-methyl-1-undecene, 2-cyclohexen-1-one, and 3,4-epoxy-1-cyclohexene (Table S2). With other substrates, instead of addition of diethyl ether, CD_3CN (1 mL) and nitrobenzene (1 equiv., internal standard) in MeCN (1 mL) were added, and the sample was subjected to NMR spectroscopic analysis (referred to as "yields determined by NMR"). The two analysis methods were compared for *cis*-4-octene: both procedures gave the same results. With 2-cyclohexen-1-one and dimethyl fumarate, the conversion was determined by GC analysis and the epoxide yield by NMR spectroscopic analysis. For the epoxidation of carvone, method A was applied, with either 0, 0.015, or 50 equiv. of MeCOOH added at the start; reactions were performed for 10, 20, 70, or 90 min and either 1.0 equiv. or 1.2 equiv. H_2O_2 was used. The carvone epoxide was isolated in order to obtain an authentic sample for comparison and quantification purposes. The isolation was performed in a similar procedure but without MeCOOH, and with a tenfold increase of the amount of the substrate (7.2 mmol) and 1.5 h reaction time.

Oxidative Cleavage Protocol, Method B: The epoxidation protocol described above for the monoalkenes (method A) was also applied for the oxidative cleavage method B. At the end of the reaction of method A (i.e. after 10 min), the reaction mixture was warmed up to 50 °C, and H_2SO_4 (0.5 equiv.) in H_2O (75 equiv.) was added, after which the mixture was stirred for 0.5 h. Then, $NaHCO_3$ (1 equiv.), $NaIO_4$ (1.5 equiv.), and H_2O (600 equiv.) were added to the reaction mixture, which was stirred for an additional 0.5 h. Subsequently, CD_3CN (1 mL), and nitrobenzene (1 equiv.) in MeCN (1 mL) were added, after which a sample was analyzed with ^1H NMR spectroscopy. For accurate determination of the conversion, after analysis with NMR spectroscopy, diethyl ether (20 mL) was added, and a sample was subjected to GC analysis. The reactions with *cis*-cyclooctene, citronellol, and citronellyl acetate were run on threefold larger scale (2.16 mmol), and isolated yields were determined by extraction with diethyl ether (3 × 20 mL), drying over $MgSO_4$, filtration, and concentration in vacuo. For the reaction with perillic acid, after concentration, the crude mixture was further purified by column chromatography to provide the pure product. The reactions with 1-dodecene and 2-methyl-undecene were additionally analyzed by GC for accurate determination of the conversion. For the reaction with dienes, a protocol similar to method B was used, the only difference being that 1.0 equiv. instead of 1.5 equiv. of H_2O_2 were utilized. For the reaction with carvone, 1.1 equiv. of H_2O_2 was used. Furthermore, at the end of the reaction, diethyl ether (20 mL) was added, followed by nitrobenzene (1 equiv.) in MeCN, and a sample was subjected to GC analysis.

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