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Alkene Epoxidation

Dirhodium(II)-Mediated Alkene Epoxidation with Iodine(III) Oxidants

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To the memory of Pierre Potier

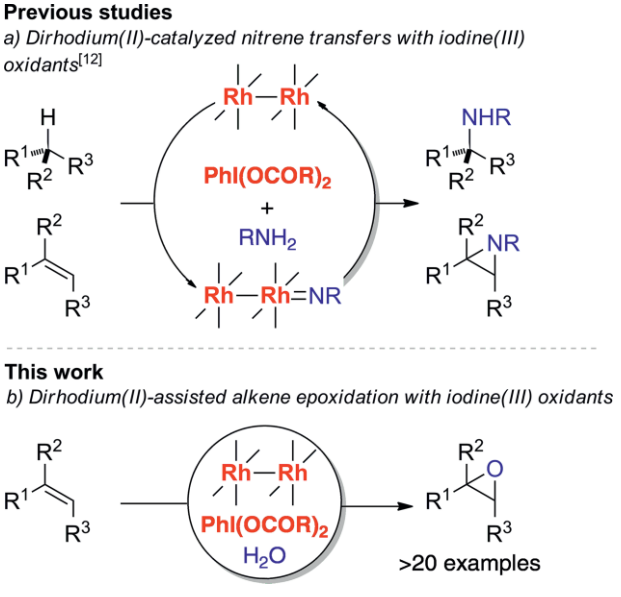
Abstract: Dirhodium(II) complexes and iodine(III) oxidants have found useful applications in synthetic nitrene chemistry. In this study, the combination of the dirhodium(II) complex $Rh_2(tpa)_4$ (tpa = triphenylacetate) with the iodine(III) oxidant $PhI(OPiv)_2$ is shown to promote the epoxidation of alkenes in the presence of 2 equivalents of water. The reaction can be applied to diversely substituted alkenes and the corresponding epoxides are isolated with yields of up to 90 %. A possible mechanism involves the dirhodium(II) complex as a Lewis acid species that would tune the oxidizing character of the iodine(III) reagent.

Introduction

Hypervalent iodine compounds are useful reagents in organic synthesis that allow for performing different types of oxidation reactions under mild conditions.[1,2] Among the functional groups likely to react with iodine(III) oxidants, alkenes are valuable platforms that give generally access to a wide range of difunctionalized products.[3] Epoxides, however, can also be obtained by the reaction of iodosylbenzene (PhI=O) with electron-deficient olefins such as enones and ketenes.[4] Similarly, Fe^{III}-, Mn^{III}-, Cr^{III}-, Ru^{II}- or Ru^{III} complexes inspired by the natural oxygenases, can react with PhI=O to generate metal-oxo species that are highly efficient agents for the epoxidation of simple alkenes.[1,5]

Use of dirhodium(II) paddlewheel complexes for the decomposition of diazo compounds has led to significant breakthroughs in synthetic carbene chemistry.[6] By comparison, their ability to mediate selective oxidation reactions has been less explored although this reactivity was first unveiled in 1982.[7] Recent studies, nevertheless, have described efficient allylic and benzylic oxidations resulting from the reaction of a dirhodium(II) complex with an oxidant such as *tert*-butylhydroperoxide.[8] Dirhodium caprolactame, particularly, has proved highly active to mediate these reactions that proceed through a radical pathway. The mechanistic investigations, then, has led to develop a dirhodium(II)-catalyzed alkene epoxidation under oxygen in the presence of isobutyraldehyde.[9]

The combination of the hypervalent iodine chemistry with the dirhodium(II) catalysis has been translated by several achievements in synthetic carbene[10] and nitrene[11] chemistry. Of particular relevance is the ability of dirhodium complexes to react with an iminoiodinane to afford a metallanitrene species. The latter allows for functionalizing different types of C(sp^3)–H bond and alkenes,[12] thereby making the dirhodium(II)-catalyzed oxidative amination reactions new efficient tools for the synthesis of nitrogen-containing natural products and bioactive compounds (Scheme 1a).[13]



Scheme 1. Background for the study.

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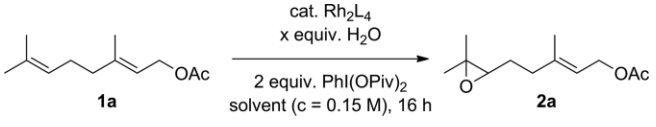
Recent investigations in our group, however, have revealed a different reactivity following the mixing of a dirhodium(II) complex and an iodine(III) oxidant. Application of reaction conditions likely to promote nitrene transfers to alkenes, thus, led us to isolate an epoxide instead of the expected aziridine (Scheme 1b). This unusual result convinced us to study further this transformation akin to a dirhodium(II)-assisted alkene epoxidation involving a trivalent iodine reagent. We, therefore, wish to report in this manuscript the results of our investigations.

Results and Discussion

In the course of our studies devoted to the search for new efficient oxidative amination processes, we have found that the reaction of geranyl acetate **1a** with a sulfamate and $PhI(OPiv)_2$ (OPiv = OCO*t*Bu) in the presence of the $Rh_2(esp)_2$ complex (esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)[14] affords a single product for which the NMR spectroscopic data clearly indicate the absence of the SO_3R motif. Careful analysis of the NMR and MS spectra, thus, revealed that the isolated compound was the terminal tri-substituted epoxide **2a**.[15] The formation of such an oxygenated product under the classical conditions for nitrene addition was puzzling and led us to explore further the reaction.

A first rapid screening of the reaction parameters in the absence of the nitrene precursor has shown that the best yields are obtained with the $Rh_2(tpa)_4$ complex (tpa = triphenylacetate) as the catalyst in dichloromethane or trifluoroethanol (see Table S1 in the Supporting Information). However, we have rapidly observed that the results strongly depend on the quality of the solvents with the presence of water being crucial for the course of the epoxidation reaction. Thus, whereas use of freshly distilled dichloromethane only leads to traces of **2a** (entry 1, Table 1), the addition of 2 equivalents of water allows for improving the conversion, the epoxide **2a** being obtained with a yield of 72 % (entry 2).

Table 1. Optimization studies for the dirhodium(II)-mediated epoxidation.



1a 2a

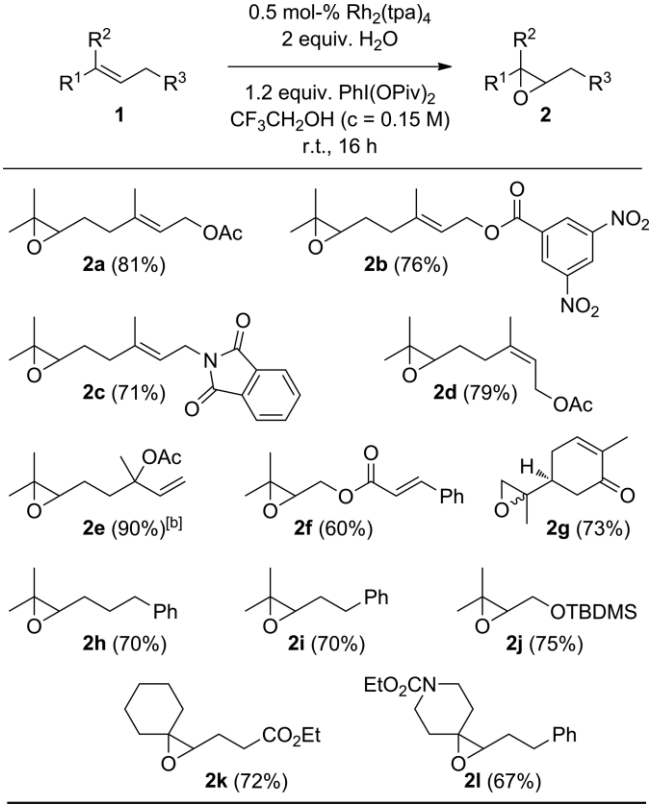
Entry	Equiv. H_2O	Catalyst [mol-%]	Solvent	Yield [%][a]
1	0	$Rh_2(tpa)_4$ (2)	DCM	<5
2	2	$Rh_2(tpa)_4$ (2)	DCM	72
3	2	$Rh_2(tpa)_4$ (2)	trifluoroethanol	83
4	1	$Rh_2(tpa)_4$ (2)	trifluoroethanol	52
5	4	$Rh_2(tpa)_4$ (2)	trifluoroethanol	83
6	2	$Rh_2(OCOC_3F_7)_4$ (2)	trifluoroethanol	40
7	2	$Rh_2(OCOC_7H_{15})_4$ (2)	trifluoroethanol	50
8	2	$Rh_2(OAc)_4$ (2)	trifluoroethanol	<10
9	2	$Rh_2(esp)_2$ (2)	trifluoroethanol	60
10	2	$Rh_2(tpa)_4$ (0.5)	trifluoroethanol	81
11	2	$Rh_2(tpa)_4$ (0.1)	trifluoroethanol	40
12[b]	2	$Rh_2(tpa)_4$ (0.5)	trifluoroethanol	81
13[c]	2	$Rh_2(tpa)_4$ (0.5)	trifluoroethanol	78

[a] Isolated yields. [b] The reaction was performed with 1.2 equiv. of $PhI(OPiv)_2$. [c] With 1.2 equiv. of $PhI(OAc)_2$.

The same observation was made with trifluoroethanol and the study performed with this solvent and 2 equivalents of H_2O led to an optimized yield of 83 % (entries 3–5). Screening of the dirhodium(II) complexes again brings to light the highest activity of $Rh_2(tpa)_4$ to mediate the epoxidation reaction (entries 6–9), a yield of 81 % being obtained using only 0.5 mol-% of this complex (entries 10 and 11). Finally, reducing the quantity of the iodine(III) oxidant to 1.2 equivalents does not modify the yield, as does the replacement of $PhI(OPiv)_2$ by $PhI(OAc)_2$ (entries 12 and 13). We have thus decided to choose the conditions displayed in entry 12 to explore the scope of the reaction.[16]

We first studied the case of tri-substituted alkenes (Table 2).[17] Various geranyl and neryl derivatives proved to react efficiently to afford selectively the corresponding monoepoxides **2a**–**d**, with yields between 71 and 81 %.[18] The selectivity probably arises from the inductive effect of the terminal carboxylate or imide that decreases the reactivity of the proximal alkene. The epoxide **2e** derived from linalyl acetate, on the other hand, highlights the higher reactivity of a tri-substituted olefin in the presence of a mono-substituted alkene. Similarly, epoxides **2f** and **2g** demonstrates that α,β-unsaturated ester and ketone do not react under these conditions.[19] Substrates **1h** and **1i**, which display a potentially oxidizable benzylic position, only led to the epoxides **2h** and **2i**. Compound **2j** shows the tolerance of the reaction towards the presence of a silyl-

Table 2. Dirhodium(II)-mediated epoxidation of tri-substituted alkenes.[a]

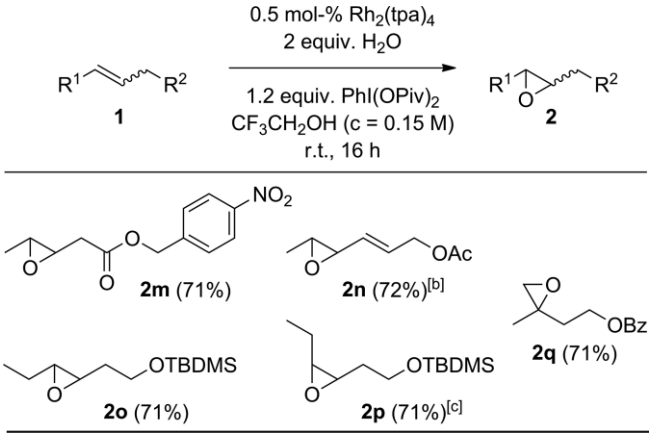


[a] Isolated yields. [b] 3 h of reaction.

protecting group. Finally, spiro derivatives **2k** and **2l** can also be obtained from cyclic alkylidene starting materials.

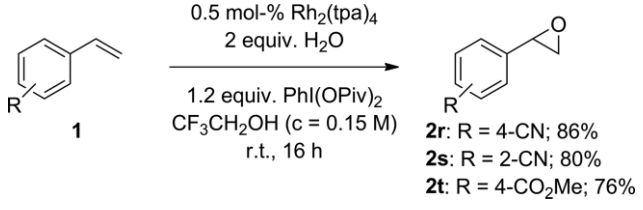
The reaction also applies to di-substituted olefins (Table 3). *Trans*-epoxides were generally isolated from the corresponding (*E*)-alkenes, except in the case of **2n** for which ^{1}H NMR shows the formation of a small amount of the *cis*-epoxide. In a similar manner, the (*Z*)-olefin **1p** leads to slight isomerization under the reaction conditions, the corresponding epoxide **2p** being isolated as a 13:1 mixture of *cis:trans* isomers. *Gem*-di-substituted alkenes are also relevant substrates for the reaction as demonstrated by compound **2q**.

Table 3. Dirhodium(II)-mediated epoxidation of di-substituted alkenes.[a]



[a] Isolated yields. [b] 4 h of reaction. Isolated as a 10:1 mixture of *trans:cis* isomers. [c] Isolated as a 13:1 mixture of *cis:trans* isomers according to the ^{1}H NMR spectroscopy.

Finally, whereas simple terminal olefins such as a protected but-3-en-1-ol do not react, aromatic alkenes can be converted to epoxides. Styrene derivatives substituted by a cyano or an ester function, thus, afford the corresponding epoxides in good yields (Scheme 2).[20] However, the reaction with styrene as well as with α- or β-substituted derivatives led to the formation of an intractable mixture of products probably resulting from the oxidative cleavage of the epoxide.[21]

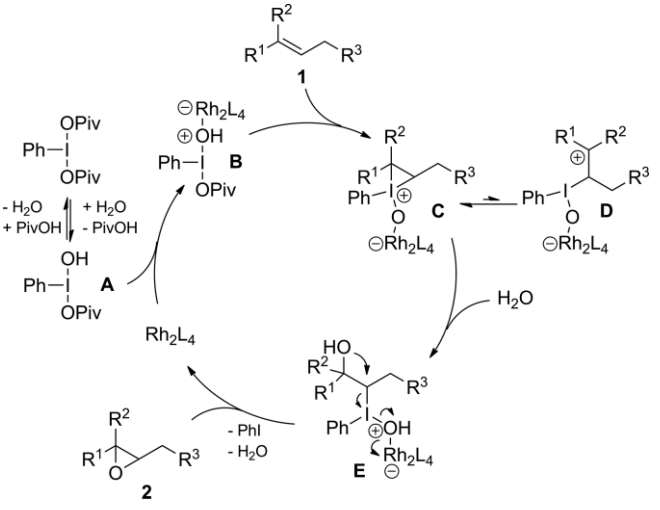


Scheme 2. Dirhodium(II)-mediated epoxidation of styrene derivatives.

Several test experiments have been made to investigate the possible mechanism for this transformation. First, the reaction performed from geranyl acetate in the absence of the dirhodium(II) complex only led to traces of the corresponding epoxide **2a**, thereby demonstrating its key role in the process.

The extensive mechanistic studies on the rhodium-catalyzed aerobic Mukaiyama epoxidation performed by Doyle, then, led us to consider the possible involvement of radicals.[9] The reaction of 2-methyl-5-phenylpent-2-ene **1i** carried out with carefully degassed trifluoroethanol affords the epoxide **2i** with a similar yield, whereas the reaction of geranyl acetate in the presence of the radical inhibitor BHT allowed us for obtaining **2a** without a noticeable change in the conversion. The hypothesis of a radical pathway was thus ruled out based on these observations.

The formation of metal-oxo species as those reported with Fe, Mn, Cr or Ru complexes,[5] is unknown with dirhodium(II) complexes to the best of our knowledge. We, therefore, propose that the latter might act as a Lewis acid species in the alkene epoxidation according to the mechanism depicted in Scheme 3.[22–24]



Scheme 3. Mechanism for the dirhodium-mediated epoxidation of alkene.

The presence of water could induce a first ligand exchange with the $PhI(OPiv)_2$ reagent to afford the iodine(III) species **A**. Then, by analogy with the acknowledged mechanism of rhodium-catalyzed nitrene transfer with iminoiodinanes,[12] we suggest that the dirhodium(II) complex react with **A** to afford the intermediate of type **B**. The latter could react with a double bond to produce the cyclic iodonium **C**[25] that could undergo sequential nucleophilic displacement with water to give the epoxide **2**, and release iodobenzene and water as by-products while regenerating the dirhodium(II) complex. This mechanistic hypothesis is in line with the lack of reactivity observed with poorly nucleophilic alkenes such as mono-substituted terminal olefins that could not add to the iodonium **B**. On the other hand, the isomerization observed in the case of compounds **2n** and **2p** could be rationalized by a hypothetical equilibrium between the intermediate **C** and the carbocationic species **D** that has been invoked in our previous study on alkene difunctionalization with rhodium-bound nitrenes.[12m]

Conclusions

This manuscript has documented an unusual reactivity arising from the combination of dirhodium(II) catalysts and iodine(III) oxidants. In the presence of a stoichiometric amount of an alkene and two equivalents of water, the reaction gives rise to

epoxides that have been isolated with yields in the 60–90 % range. Accordingly, this method could provide an alternative to classical methods for epoxidation involving, for example, the use of *m*-CPBA. The transformation applies to tri-, di-, and mono-substituted alkenes that display a nucleophilic character. Since this unusual reactivity was initially noticed under conditions for catalytic nitrene additions, it should be considered as a possible side reaction in further studies centered on allylic amination or alkene aziridination.

Experimental Section

General Procedure for the Epoxidation Reaction: A flask containing the substrate (200 μmol, 1.00 equiv.) was charged with $Rh_2(tpa)_4$ (1.40 mg, 1.00 μmol, 0.5 mol-%) and 1.30 mL of 2,2,2-trifluoroethanol. To this mixture were added $PhI(OPiv)_2$ (97.5 mg, 240 μmol, 1.20 equiv.) in one portion, and, then, H_2O (7.20 μL, 400 μmol, 2.00 equiv.). The mixture was stirred between 4 and 16 h at room temperature. After concentration under reduced pressure, the residue was purified by flash chromatography on silica gel.

(*E*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl Acetate (2a):[26] Prepared according to the general procedure for epoxidation using **1a** (39.2 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2a** was obtained as a colorless oil (35.2 mg, 81 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.39 (t, *J* = 6.8 Hz, 1 H), 4.59 (d, *J* = 6.8 Hz, 2 H), 2.70 (t, *J* = 6.0 Hz, 1 H), 2.30–2.10 (m, 2 H), 2.05 (s, 3 H), 1.73 (s, 3 H), 1.70–1.63 (m, 2 H), 1.31 (s, 3 H), 1.26 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, 141.4, 119.0, 64.0, 61.3, 58.5, 36.3, 27.1, 24.9, 21.1, 18.8, 16.5 ppm.

(*E*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl 3,5-Dinitro-benzoate (2b):[27] Prepared according to the general procedure for epoxidation using **1b** (69.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2b** was obtained as a yellow solid (55.0 mg, 76 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.22 (t, *J* = 2.1 Hz, 1 H), 9.16 (d, *J* = 2.1 Hz, 2 H), 5.57–5.52 (m, 1 H), 4.98 (d, *J* = 7.3 Hz, 2 H), 2.72 (dd, *J* = 6.9, 5.5 Hz, 1 H), 2.34–2.19 (m, 2 H), 1.84 (s, 3 H), 1.77–1.64 (m, 2 H), 1.31 (s, 3 H), 1.28 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7, 148.8 (2 C), 143.7, 134.3, 129.6 (2 C), 122.4, 117.8, 63.9, 63.7, 58.5, 36.5, 27.2, 25.0, 18.9, 16.8 ppm.

(*E*)-2-[5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl]isoindoline-1,3-dione (2c):[28] Prepared according to the general procedure for epoxidation using **1c** (57.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2c** was obtained as a white powder (42.0 mg, 70 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.80 (m, 2 H), 7.70 (dd, *J* = 4.9, 3.2 Hz, 2 H), 5.31 (t, *J* = 7.0 Hz, 1 H), 4.29 (d, *J* = 7.0 Hz, 2 H), 2.67 (t, *J* = 6.2 Hz, 1 H), 2.26–2.05 (m, 2 H), 1.85 (s, 3 H), 1.69–1.57 (m, 2 H), 1.26 (s, 3 H), 1.24 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2 (2 C), 139.9, 134.0 (2 C), 132.4 (2 C), 123.3 (2 C), 118.8, 64.0, 58.5, 36.3, 35.9, 27.2, 24.9, 18.8, 16.5 ppm.

(*Z*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl Acetate (2d):[29] Prepared according to the general procedure for epoxidation using nerol acetate (39.2 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2d** was obtained as a colorless oil (35.2 mg, 79 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.41 (t, *J* = 7.1 Hz, 1 H), 4.59 (d, *J* = 7.1 Hz, 2 H), 2.71 (t, *J* = 6.2 Hz, 1 H), 2.32–2.20 (m, 2 H), 2.05 (s, 3 H), 1.79 (s, 3 H), 1.73–1.54 (m, 2 H), 1.31 (s, 3 H), 1.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, 141.8, 119.9, 73.9, 61.0, 58.5, 29.0, 27.7, 25.0, 23.6, 21.2, 18.8 ppm.

5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-1-en-3-yl Acetate (2e):[9] Prepared according to the general procedure for epoxidation using **1e** (39.2 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2e** was obtained as a colorless oil (38.0 mg, 90 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.04–5.88 (m, 1 H), 5.25–5.07 (m, 2 H), 2.71 (t, *J* = 6.2 Hz, 1 H), 2.01 (s, 3 H), 1.95–1.85 (m, 2 H), 1.55 (d, *J* = 6.9 Hz, 3 H), 1.68–1.40 (m, 2 H), 1.31 (s, 3 H), 1.25 (d, *J* = 5.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.0, 141.6, 141.4, 113.7, 113.6, 82.6, 82.5, 64.1, 58.5, 36.4, 25.0, 23.8, 23.7, 23.6, 22.3, 18.7 ppm.

(3,3-Dimethyloxiran-2-yl)methyl Cinnamate (2f): Prepared according to the general procedure for epoxidation using **1f** (43.2 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt) **2f** was obtained as a colorless liquid (27.6 mg, 60 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.70 (m, 1 H), 7.55–7.51 (m, 2 H), 7.41–7.38 (m, 3 H), 6.48 (d, *J* = 16.1 Hz, 1 H), 4.49 (dd, *J* = 12.1, 4.2 Hz, 1 H), 4.15 (dd, *J* = 12.1, 6.8 Hz, 1 H), 3.11–3.05 (m, 1 H), 1.38 (s, 3 H), 1.37 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 145.6, 134.4, 130.5, 129.0 (2 C), 128.3 (2 C), 117.6, 63.6, 60.7, 58.2, 24.7, 19.1 ppm. IR (neat): $\tilde{\nu}$ = 2962, 2928, 1712, 1635, 1526, 1451, 1351, 1307, 1254, 1165, 1133 cm^{-1}. HRMS = $[M + H]^+$ calculated for $[C_{14}H_{17}O_3]^+$ = 233.1172, found 233.1176.

(*R*)-2-Methyl-5-[(*R*)-2-methyloxiran-2-yl]cyclohex-2-en-1-one (2g):[30] Prepared according to the general procedure for epoxidation using (*R*)-Carvone (30.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), 5 was obtained as a yellow oil (24.1 mg, 73 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74 (s, 1 H), 2.69 (dd, *J* = 11.0, 4.5 Hz, 1 H), 2.63–2.57 (m, 2 H), 2.50–2.33 (m, 2 H), 2.33–2.14 (m, 2 H), 1.78 (s, 3 H), 1.32 (d, *J* = 5.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 144.3, 144.0, 135.7, 58.1, 58.0, 53.1, 52.5, 41.5, 40.8, 40.5, 40.1, 28.0, 27.8, 19.2, 18.5, 15.8 ppm.

2,2-Dimethyl-3-(3-phenylpropyl)oxirane (2h): Prepared according to the general procedure for epoxidation using **1h** (35.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2h** was obtained as a colorless liquid (26.0 mg, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 3 H), 7.19 (d, *J* = 6.6 Hz, 2 H), 2.74 (dd, *J* = 11.4, 5.0 Hz, 1 H), 2.70–2.63 (m, 2 H), 1.93–1.66 (m, 2 H), 1.62–1.52 (m, 2 H), 1.30 (s, 3 H), 1.24 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.2, 128.5 (2 C), 128.4 (2 C), 125.9, 64.4, 58.31 35.8, 28.6, 28.5, 25.0, 18.8 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2921, 2860, 1496, 1455, 1376, 1283, 1249, 1153, 1114, 890, 745, 697 cm^{-1}. HRMS = $[M + H]^+$ calculated for $[C_{13}H_{19}O]^+$ = 191.1430, found 191.1442.

2,2-Dimethyl-3-phenethyloxirane (2i):[31] Prepared according to the general procedure for epoxidation using **1i** (32.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2i** was obtained as a white solid (25.0 mg, 72 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (m, 3 H), 7.20 (d, *J* = 6.0 Hz, 2 H), 2.92–2.64 (m, 3 H), 1.99–1.73 (m, 2 H), 1.27 (s, 3 H),

1.12 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 128.6 (2 C), 128.5 (2 C), 126.2, 64.0, 58.7, 32.9, 30.9, 24.9, 18.7 ppm.

***tert*-Butyl[(3,3-dimethyloxiran-2-yl)methoxy]dimethylsilane (2j):**[32] Prepared according to the general procedure for epoxidation using **1j** (40.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2j** was obtained as a colorless oil (32.4 mg, 75 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (d, *J* = 5.3 Hz, 2 H), 2.90 (t, *J* = 5.3 Hz, 1 H), 1.34 (s, 3 H), 1.28 (s, 3 H), 0.91 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.2, 62.5, 58.3, 26.0 (3 C), 25.0 (2 C), 19.0, –5.0, –5.2 ppm.

Ethyl 3-(1-Oxaspiro[2.5]octan-2-yl)propanoate (2k): Prepared according to the general procedure for epoxidation using **1k** (39.3 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2k** was obtained as a colorless oil (30.0 mg, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.15 (q, *J* = 7.1 Hz, 2 H), 2.80–2.72 (m, 1 H), 2.48 (dd, *J* = 11.8, 7.6 Hz, 2 H), 2.00–1.63 (m, 4 H), 1.62–1.47 (m, 8 H), 1.26 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.6, 60.5, 51.3, 43.1, 32.2, 31.7, 29.5, 28.7, 27.4, 24.4 (1 C, 1 C), 14.4 ppm. IR (neat): $\tilde{\nu}$ = 2928, 2860, 1736, 1690, 1455, 1375, 1275, 1169, 1123, 1031, 934 cm^{-1}. HRMS = $[M + H]^+$ calculated for $[C_{12}H_{21}O_3]^+$ = 213.1485, found 213.1471.

Ethyl 2-Phenethyl-1-oxa-6-azaspiro[2.5]octane-6-carboxylate (2l): Prepared according to the general procedure for epoxidation using **1l** (55.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2l** was obtained as a colorless oil (38.0 mg, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 2 H), 7.24–7.16 (m, 3 H), 4.14 (q, *J* = 6.4 Hz, 2 H), 3.82–3.62 (m, 2 H), 3.44–3.26 (m, 2 H), 2.88–2.82 (m, 2 H), 2.80–2.65 (m, 1 H), 2.02–1.67 (m, 4 H), 1.52–1.31 (m, 2 H), 1.26 (t, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 141.2, 128.7 (2 C), 128.6 (2 C), 126.4, 63.9, 61.5, 61.1, 42.2, 42.3, 34.6, 32.8, 30.0, 29.0, 14.8 ppm. IR (neat): $\tilde{\nu}$ = 2962, 2931, 2863, 1693, 1428, 1378, 1275, 1229, 1169, 1125, 1093, 1069, 1026, 890, 764, 749, 698 cm^{-1}. HRMS = $[M + H]^+$ calculated for $[C_{17}H_{24}NO_3]^+$ = 290.1750, found 290.1780.

4-Nitrobenzyl 2-(3-Methyloxiran-2-yl)acetate (2m): Prepared according to the general procedure for epoxidation using **1m** (47.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2m** was obtained as a colorless oil (35.5 mg, 71 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.3 Hz, 2 H), 7.53 (d, *J* = 8.3 Hz, 2 H), 5.26 (s, 2 H), 3.05 (d, *J* = 4.4 Hz, 1 H), 2.89–2.82 (m, 1 H), 2.65 (ddd, *J* = 22.9, 16.4, 5.6 Hz, 2 H), 1.34 (d, *J* = 5.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 143.0, 128.5 (2 C), 124.0 (2 C), 65.2, 54.8, 54.6, 37.7, 17.4 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2921, 2860, 1550, 1475, 1455, 1376, 1283, 1249, 1153, 1114, 890, 745 cm^{-1}. HRMS = $[M + H]^+$ calculated for $[C_{12}H_{14}NO_5]^+$ = 252.0876, found 252.0866.

***(E)*-3-(3-Methyloxiran-2-yl)allyl Acetate (2n):**[33] Prepared according to the general procedure for epoxidation using *trans*,*trans*-2,4-hexadienyl acetate (28.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2n** was obtained as a mixture of 10:1 *trans:cis* isomers, and as a colorless oil (22.5 mg, 72 %). Only the major diastereoisomer is described for clarity. The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.07–5.90 (m, 1 H), 5.51 (dd, *J* = 15.4, 7.9 Hz, 1 H), 4.58 (d, *J* = 5.9 Hz, 2 H), 3.11 (dd, *J* = 14.9, 7.2 Hz, 1 H), 2.92 (d, *J* = 5.1 Hz, 1 H), 2.08 (s, 3 H), 1.35 (d, *J* = 5.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.6, 132.0, 128.8, 64.0, 58.6, 56.7, 21.0, 17.6 ppm.

***(3R*,4R*)*-*tert*-Butyl[2-(3-ethyloxiran-2-yl)ethoxy]dimethylsilane (2o):**[34] Prepared according to the general procedure for epoxidation using **1o** (42.9 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2o** was obtained as a white powder (32.7 mg, 71 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (dd, *J* = 6.3, 6.0 Hz, 2 H), 2.81 (td, *J* = 6.0, 2.4 Hz, 1 H), 2.69 (td, *J* = 5.4, 2.4 Hz, 1 H), 1.82–1.63 (dt, *J* = 12.9, 6.6 Hz, 2 H), 1.57 (m, 2 H), 1.07 (t, *J* = 7.5 Hz, 3 H), 0.92 (s, 9 H), 0.09 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 60.2 (2 C), 56.2, 35.7, 26.0 (3 C), 25.3, 18.4, 10.0, –5.2 (2 C) ppm.

***(3R*,4S*)*-*tert*-Butyl[2-(3-ethyloxiran-2-yl)ethoxy]dimethylsilane (2p):**[35] Prepared according to the general procedure for epoxidation using **1p** (42.9 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2p** was obtained as a mixture of 13:1 *cis:trans* isomers, and as a colorless liquid (32.7 mg, 71 %). Only the major diastereoisomer is described for clarity. The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.81–3.77 (m, 2 H), 3.09–3.04 (m, 1 H), 2.93–2.88 (m, 1 H), 1.84–1.74 (m, 1 H), 1.72–1.63 (m, 1 H), 1.61–1.47 (m, 2 H), 1.05 (t, *J* = 7.5 Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 60.7, 58.4, 54.9, 31.3, 26.0 (3 C), 21.4, 18.5, 10.7, –5.2 (2 C) ppm.

2-(2-Methyloxiran-2-yl)ethyl Benzoate (2q):[36] Prepared according to the general procedure for epoxidation using **1q** (32.4 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2q** was obtained as a brown powder (25.0 mg, 71 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.8 Hz, 2 H), 7.57 (t, *J* = 7.1 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 4.54–4.36 (m, 2 H), 2.72 (d, *J* = 4.7 Hz, 1 H), 2.64 (d, *J* = 4.7 Hz, 1 H), 2.18–1.94 (m, 2 H), 1.42 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 133.2, 129.7 (2 C), 129.4, 128.6 (2 C), 74.4, 61.6, 59.9, 35.9, 21.5 ppm.

4-(Oxiran-2-yl)benzonitrile (2r):[37] Prepared according to the general procedure for epoxidation using **1r** (28.8 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2r** was obtained as a white powder (24.5 mg, 85 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 2 H), 7.39 (d, *J* = 7.8 Hz, 2 H), 3.91 (dd, *J* = 2.5, 4.0 Hz, 1 H), 3.21 (dd, *J* = 5.4, 4.2 Hz, 1 H), 2.76 (dd, *J* = 5.5, 2.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.0, 132.5 (2 C), 126.3 (2 C), 118.7, 112.1, 51.7 (2 C) ppm.

2-(Oxiran-2-yl)benzonitrile (2s):[37] Prepared according to the general procedure for epoxidation using **1s** (26.0 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2s** was obtained as a white powder (23.0 mg, 80 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.6 Hz, 1 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 7.34 (d, *J* = 7.6 Hz, 1 H), 4.25 (s, 1 H), 3.29–3.24 (m, 1 H), 2.78–2.73 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.5 (2 C), 132.9 (2 C), 128.6, 125.0, 101.8, 51.6, 50.5 ppm.

Methyl 4-(oxiran-2-yl)benzoate (2t):[38] Prepared according to the general procedure for epoxidation using **1t** (32.4 mg, 200 μmol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2t** was obtained as a white powder (27.0 mg, 76 %). The ^{1}H NMR spectrum is in accordance with the literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.7 Hz, 1 H), 7.38 (d, *J* = 7.7 Hz, 1 H), 3.95 (s, 4 H), 3.25–3.19 (m, 1 H), 2.87–

2.79 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 143.0, 130.0 (2 C), 126.9, 125.6 (2 C), 52.3, 52.0, 51.6 ppm.

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[17] The reaction with a tetrasubstituted alkene only leads to the recovery of the starting material.

[18] An allylic alcohol such as geraniol does not afford the corresponding epoxide under the reaction conditions. A complex mixture of products, instead, is obtained as indicated by the ^1H NMR of the crude.

[19] In order to circumvent the lack of reactivity of α,β-unsaturated ketones, these were converted to cyclic ketals. However, application of the reaction conditions to the latter only leads to the starting ketone following cleavage of the ketal.

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Alkene Epoxidation

The combination of rhodium(II) catalysis and iodine(III) oxidant, which is well acknowledged for inducing nitrogen atom transfer, is shown to promote an unusual alkene epoxidation in the presence of water. The reaction involves a Lewis acidic dirhodium(II) complex bound to an iodonium species that would undergo nucleophilic displacement with water.

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