



HAL
open science

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

Ali Nasrallah, Gwendal Grelier, Maria Ivana Lapuh, Fernando J Duran, Benjamin Darses, Philippe Dauban

► **To cite this version:**

Ali Nasrallah, Gwendal Grelier, Maria Ivana Lapuh, Fernando J Duran, Benjamin Darses, et al.. Dirhodium(II)-Mediated Alkene Epoxidation with Iodine(III) Oxidants. *European Journal of Organic Chemistry*, 2018, 2018 (42), pp.5836-5842. 10.1002/ejoc.201800306 . hal-02366218

HAL Id: hal-02366218

<https://hal.science/hal-02366218>

Submitted on 15 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Dirhodium(II)-mediated alkene epoxidation with iodine(III) oxidants

Ali Nasrallah,^[a] Gwendal Grelier,^[a] Maria Ivana Lapuh,^[a,b] Fernando J. Duran,^[b] Benjamin Darses,^[a] and Philippe Dauban*^[a]

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 $\text{Rh}_2(\text{tpa})_4$ with the iodine(III) oxidant $\text{PhI}(\text{OPiv})_2$ 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 would involve 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 ($\text{PhI}=\text{O}$) 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 $\text{PhI}=\text{O}$ 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 rhodium(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

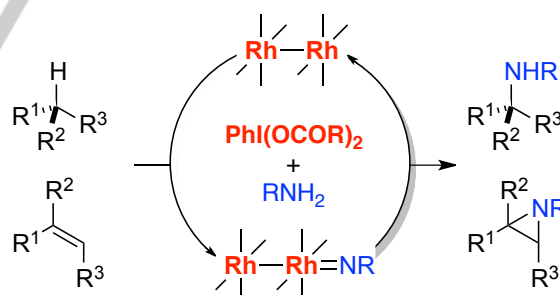
rhodium(II)-catalyzed alkene epoxidation under oxygen in the presence of isobutyraldehyde.^[9]

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 $\text{C}(\text{sp}^3)\text{—H}$ 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]

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.

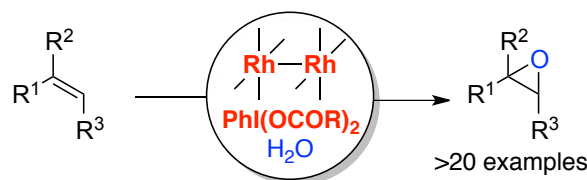
Previous studies

a) Dirhodium(II)-catalyzed nitrene transfers with iodine(III) oxidants^[12]



This work

b) Dirhodium(II)-assisted alkene epoxidation with iodine(III) oxidants

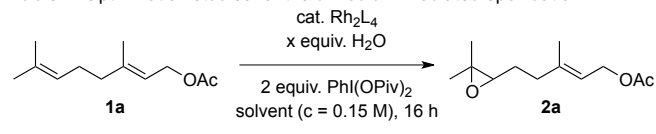


Scheme 1. Background for the study.

[a] A. Nasrallah, G. Grelier, M. I. Lapuh, Dr. B. Darses, Dr. P. Dauban Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Univ. Paris-Sud, Université Paris-Saclay, 1, av. de la Terrasse, 91198 Gif-sur-Yvette (France).
E-mail: philippe.dauban@cnrs.fr

[b] M. I. Lapuh, Prof. F. J. Duran Departamento de Química Orgánica and UMYMFOR (CONICET-UBA), Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires (Argentina)

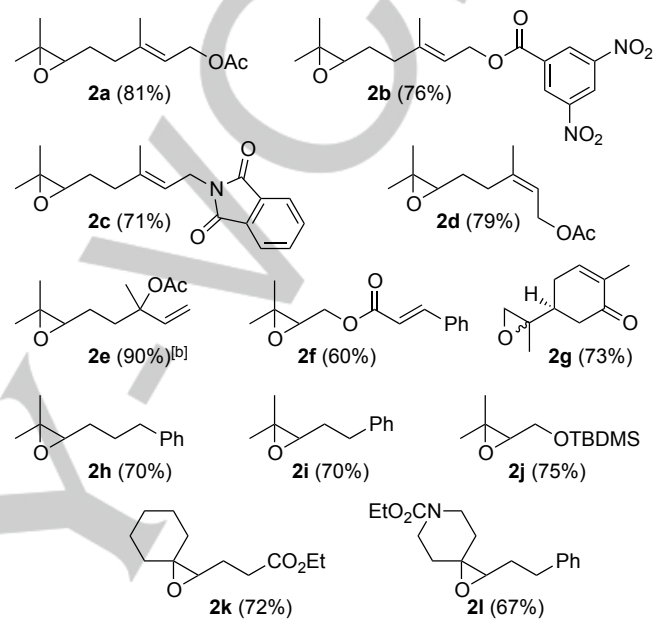
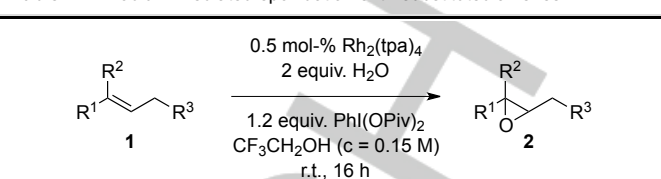
Results and Discussion

Table 1. Optimization studies for the dirhodium-mediated epoxidation.

Entry	Equiv. H ₂ O	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 ₃ F ₇) ₄ (2)	Trifluoroethanol	40
7	2	Rh ₂ (OCOC ₇ H 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 equivalents of PhI(OPiv)₂. [c] With 1.2 equivalents of PhI(OAc)₂.

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 Rh₂(esp)₂ complex (esp = $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedipropionic acid)^[14] affords a single product for which the NMR data clearly indicate the absence of the SO₃R 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 Rh₂(tpa)₄ complex (tpa = triphenylacetate) as the catalyst in dichloromethane or trifluoroethanol (see Table S1 in 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).

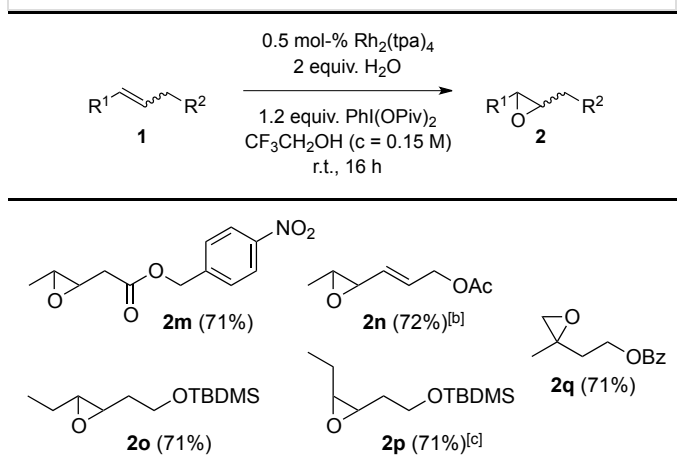
Table 2. Dirhodium-mediated epoxidation of tri-substituted alkenes.^[a]

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

The same observation was made with trifluoroethanol and the study performed with this solvent and 2 equivalents of H₂O led to an optimized yield of 83% (entries 3-5). Screening of the dirhodium(II) complexes again brings to light the highest activity of Rh₂(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 mono-epoxides **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-protecting group. Finally, spiro derivatives **2k** and **2l** can also be obtained from cyclic alkylidene starting materials.

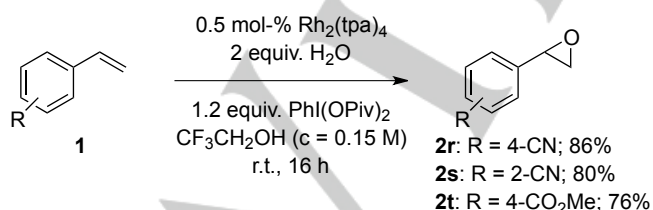
Table 3. Dirhodium-mediated epoxidation of di-substituted alkenes.^[a]



[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 ¹H NMR.

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 ¹H NMR shows the formation of a small amount of the *cis*-epoxide. In a similar manner, the *cis*-olefin **1p** slightly isomerizes 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**.

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-mediated epoxidation of styrene derivatives.

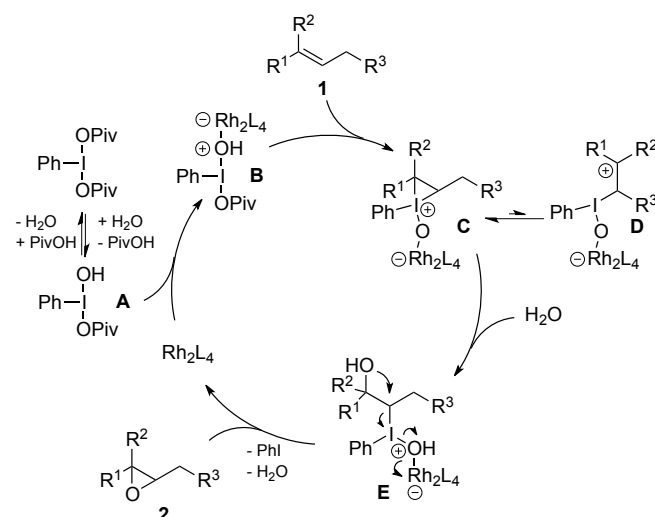
Several test experiments have been made to investigate the possible mechanism for this transformation. First, the reaction performed from geranyl acetate in the absence of the

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.^[22,23,24]

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]



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

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 eq.) was charged with $\text{Rh}_2(\text{tpa})_4$ (1.40 mg, 1.00 μmol , 0.5 mol-%) and 1.30 mL of 2,2,2-trifluoroethanol. To this mixture were added $\text{Ph}(\text{OPiv})_2$ (97.5 mg, 240 μmol , 1.20 eq.) in one portion, and, then, H_2O (7.20 μL , 400 μmol , 2.00 eq.). 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 (9/01 petroleum ether/AcOEt), **2a** was obtained as a colorless oil (35.2 mg, 81 %). The ^1H NMR spectrum is in accordance with the literature. ^1H NMR (500 MHz, CDCl_3) δ 5.39 (t, J = 6.8 Hz, 1H), 4.59 (d, J = 6.8 Hz, 2H), 2.70 (t, J = 6.0 Hz, 1H), 2.30 – 2.10 (m, 2H), 2.05 (s, 3H), 1.73 (s, 3H), 1.70 – 1.63 (m, 2H), 1.31 (s, 3H), 1.26 (s, 3H) 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-dinitrobenzoate (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 ^1H NMR spectrum is in accordance with the literature. ^1H NMR (500 MHz, CDCl_3) δ 9.22 (t, J = 2.1 Hz, 1H), 9.16 (d, J = 2.1 Hz, 2H), 5.57-5.52 (m, 1H), 4.98 (d, J = 7.3 Hz, 2H), 2.72 (dd, J = 6.9, 5.5 Hz, 1H), 2.34 – 2.19 (m, 2H), 1.84 (s, 3H), 1.77 – 1.64 (m, 2H), 1.31 (s, 3H), 1.28 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 162.7, 148.8 (2C), 143.7, 134.3, 129.6 (2C), 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 white powder (42.0 mg, 70 %). The ^1H NMR spectrum is in accordance with the literature. ^1H NMR (300 MHz, CDCl_3) δ 7.88 – 7.80 (m, 2H), 7.70 (dd, J = 4.9, 3.2 Hz, 2H), 5.31 (t, J = 7.0 Hz, 1H), 4.29 (d, J = 7.0 Hz, 2H), 2.67 (t, J = 6.2 Hz, 1H), 2.26 – 2.05 (m, 2H), 1.85 (s, 3H), 1.69 – 1.57 (m, 2H), 1.26 (s, 3H), 1.24 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl_3) δ 168.2 (2C), 139.9, 134.0 (2C), 132.4 (2C), 123.3 (2C), 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 (9/01 petroleum ether/AcOEt), **2d** was obtained as a colorless oil (35.2 mg, 79 %). The ^1H NMR spectrum is in accordance with the literature. ^1H NMR (300 MHz, CDCl_3) δ 5.41 (t, J = 7.1 Hz, 1H), 4.59 (d, J = 7.1 Hz, 2H), 2.71 (t, J = 6.2 Hz, 1H), 2.32 – 2.20 (m, 2H), 2.05 (s, 3H), 1.79 (s, 3H), 1.73 – 1.54 (m, 2H), 1.31 (s, 3H), 1.27 (s, 3H) 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 ^1H NMR spectrum is in accordance with the literature. ^1H NMR (300 MHz, CDCl_3) δ 6.04 – 5.88 (m, 1H), 5.25 – 5.07 (m, 2H), 2.71 (t, J = 6.2 Hz, 1H), 2.01 (s, 3H), 1.95 – 1.85 (m, 2H), 1.55 (d, J = 6.9 Hz, 3H), 1.68 – 1.40 (m, 2H), 1.31 (s, 3H), 1.25 (d, J = 5.3 Hz, 3H) 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 %). ^1H NMR (300 MHz, CDCl_3) δ 7.77 – 7.70 (m, 1H), 7.55 – 7.51 (m, 2H), 7.41 – 7.38 (m, 3H), 6.48 (d, J = 16.1 Hz, 1H), 4.49 (dd, J = 12.1, 4.2 Hz, 1H), 4.15 (dd, J = 12.1, 6.8 Hz, 1H), 3.11 – 3.05 (m, 1H), 1.38 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 166.9, 145.6, 134.4, 130.5, 129.0 (2C), 128.3 (2C), 117.6, 63.6, 60.7, 58.2, 24.7, 19.1 ppm. IR(neat) ν = 2962, 2928, 1712, 1635, 1526, 1451, 1351, 1307, 1254, 1165, 1133 cm^{-1} . HRMS = $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{14}\text{H}_{17}\text{O}_3]^+$ = 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), **2g** was obtained as a yellow oil (24.1 mg, 73 %). The ^1H NMR spectrum is in accordance with the literature. ^1H NMR (300 MHz, CDCl_3) δ 6.74 (s, 1H), 2.69 (dd, J = 11.0, 4.5 Hz, 1H), 2.63 – 2.57 (m, 2H), 2.50 – 2.33 (m, 2H), 2.33 – 2.14 (m, 2H), 1.78 (s, 3H), 1.32 (d, J = 5.0 Hz, 3H) 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 colorless liquid (26.0 mg, 70 %). ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.25 (m, 3H), 7.19 (d, J = 6.6 Hz, 2H), 2.74 (dd, J = 11.4, 5.0 Hz, 1H), 2.70 – 2.63 (m, 2H), 1.93 – 1.66 (m, 2H), 1.62 – 1.52 (m, 2H), 1.30 (s, 3H), 1.24 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 142.2, 128.5 (2C), 128.4 (2C), 125.9, 64.4, 58.31 35.8, 28.6, 28.5, 25.0, 18.8 ppm. IR(neat) ν = 2959, 2921, 2860, 1496, 1455, 1376, 1283, 1249, 1153, 1114, 890, 745, 697 cm^{-1} . HRMS = $[\text{M}+\text{H}]^+$ calculated for $[\text{C}_{13}\text{H}_{19}\text{O}]^+$ = 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 μ mol) 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 ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 7.28 (m, 3H), 7.20 (d, J = 6.0 Hz, 2H), 2.92 – 2.64 (m, 3H), 1.99 – 1.73 (m, 2H), 1.27 (s, 3H), 1.12 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 141.6, 128.6 (2C), 128.5 (2C), 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 μ mol) 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 ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 3.74 (d, J = 5.3 Hz, 2H), 2.90 (t, J = 5.3 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 64.2, 62.5, 58.3, 26.0 (3C), 25.0 (2C), 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 μ mol) 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 %). ¹H NMR (300 MHz, CDCl₃) δ 4.15 (q, J = 7.1 Hz, 2H), 2.80 – 2.72 (m, 1H), 2.48 (dd, J = 11.8, 7.6 Hz, 2H), 2.00 – 1.63 (m, 4H), 1.62 – 1.47 (m, 8H), 1.26 (t, J = 7.0 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 173.6, 60.5, 51.3, 43.1, 32.2, 31.7, 29.5, 28.7, 27.4, 24.4 (1C + 1C), 14.4 ppm. IR(neat) ν = 2928, 2860, 1736, 169, 1455, 1375, 1275, 1169, 1123, 1031, 934 cm⁻¹. HRMS = [M+H]⁺ calculated for [C₁₂H₂₁O₃]⁺ = 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 μ mol) 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 %). ¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 4.14 (q, J = 6.4 Hz, 2H), 3.82 – 3.62 (m, 2H), 3.44 – 3.26 (m, 2H), 2.88 – 2.82 (m, 2H), 2.80 – 2.65 (m, 1H), 2.02 – 1.67 (m, 4H), 1.52 – 1.31 (m, 2H), 1.26 (t, J = 6.4 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 155.6, 141.2, 128.7 (2C), 128.6 (2C), 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) ν = 2962, 2931, 2863, 1693, 1428, 1378, 1275, 1229, 1169, 1125, 1093, 1069, 1026, 890, 764, 749, 698 cm⁻¹. HRMS = [M+H]⁺ calculated for [C₁₇H₂₄NO₃]⁺ = 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 μ mol) 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 %). ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 5.26 (s, 2H), 3.05 (d, J = 4.4 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.65 (ddd, J = 22.9, 16.4, 5.6 Hz, 2H), 1.34 (d, J = 5.0 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 170.2, 143.0, 128.5 (2C), 124.0 (2C), 65.2, 54.8, 54.6, 37.7, 17.4 ppm. IR(neat) ν = 2959, 2921, 2860, 1550, 1475, 1455, 1376, 1283, 1249, 1153, 1114, 890, 745 cm⁻¹. HRMS = [M+H]⁺ calculated for [C₁₂H₁₄NO₅]⁺ = 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 μ mol) 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 ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 6.07 – 5.90 (m, 1H), 5.51 (dd, J = 15.4, 7.9 Hz, 1H), 4.58 (d, J = 5.9 Hz, 2H), 3.11 (dd, J = 14.9, 7.2 Hz, 1H), 2.92 (d, J = 5.1 Hz, 1H), 2.08 (s, 3H), 1.35 (d, J = 5.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) 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 μ mol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2o** was obtained as white powder (32.7 mg, 71 %). The ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 3.75 (dd, J = 6.3, 6.0 Hz, 2H), 2.81 (td, J = 6.0, 2.4 Hz, 1H), 2.69 (td, J = 5.4, 2.4 Hz, 1H), 1.82-1.63 (dt, J = 12.9, 6.6 Hz, 2H), 1.57 (m, 2H), 1.07 (t, J = 7.5 Hz, 3H), 0.92 (s, 9H), 0.09 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 60.2 (2C), 56.2, 35.7, 26.0 (3C), 25.3, 18.4, 10.0, -5.2 (2C) 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 μ mol) 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 ¹H NMR spectrum is in accordance with the literature. ¹H NMR (500 MHz, CDCl₃) δ 3.81 – 3.77 (m, 2H), 3.09 – 3.04 (m, 1H), 2.93 – 2.88 (m, 1H), 1.84 – 1.74 (m, 1H), 1.72 – 1.63 (m, 1H), 1.61 – 1.47 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 60.7, 58.4, 54.9, 31.3, 26.0 (3C), 21.4, 18.5, 10.7, -5.2 (2C) ppm.

2-(2-Methyloxiran-2-yl)ethyl benzoate (2q):^[36] Prepared according to the general procedure for epoxidation using **1q** (32.4 mg, 200 μ mol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2q** was obtained as brown powder (25.0 mg, 71 %). The ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.1 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 4.54 – 4.36 (m, 2H), 2.72 (d, J = 4.7 Hz, 1H), 2.64 (d, J = 4.7 Hz, 1H), 2.18 – 1.94 (m, 2H), 1.42 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 166.7, 133.2, 129.7 (2C), 129.4, 128.6 (2C), 74.4, 61.6, 59.9, 35.9, 21.5 ppm.

4-(Oxiran-2-yl)benzotrile (2r):^[37] Prepared according to the general procedure for epoxidation using **1r** (28.8 mg, 200 μ mol) as the starting material. After purification by flash chromatography on silica gel (9.5:0.5 petroleum ether/AcOEt), **2r** was obtained as white powder (24.5 mg, 85 %). The ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 3.91 (dd, J = 2.5, 4.0 Hz, 1H), 3.21 (dd, J = 5.4, 4.2 Hz, 1H), 2.76 (dd, J = 5.5, 2.4 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 144.0, 132.5 (2C), 126.3 (2C), 118.7, 112.1, 51.7 (2C) ppm.

2-(Oxiran-2-yl)benzotrile (2s):^[37] Prepared according to the general procedure for epoxidation using **1s** (26.0 mg, 200 μ mol) as the starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2s** was obtained as white powder (23.0 mg, 80 %). The ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 4.25 (s, 1H), 3.29 – 3.24 (m, 1H), 2.78 – 2.73 (m, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 133.5 (2C), 132.9 (2C), 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 μ mol) as the

starting material. After purification by flash chromatography on silica gel (9:1 petroleum ether/AcOEt), **2t** is obtained as white powder (27.0 mg, 76 %). The ¹H NMR spectrum is in accordance with the literature. ¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 3.95 (s, 4H), 3.25 – 3.19 (m, 1H), 2.87 – 2.79 (m, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 166.9, 143.0, 130.0 (2C), 126.9, 125.6 (2C), 52.3, 52.0, 51.6 ppm.

Acknowledgements

We wish to thank the French National Research Agency (program n° ANR-11-IDEX-0003-02, CHARMMMAT ANR-11-LABX-0039, and ANR-15-CE29-0014-01; fellowship to A. N.), the Ministère de l'Enseignement Supérieur et de la Recherche (fellowship to G. G.), the Saint Exupéry Program (grant to M. I. H.), the ECOS-Sud Committee (Action A15E04), and the Institut de Chimie des Substances Naturelles for their support.

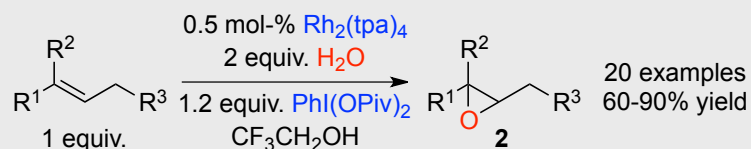
Keywords: Hypervalent iodine • rhodium • epoxidation • alkene • Lewis acid

- [1] For relevant general reviews, see: a) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123; b) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523; c) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299; d) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328; e) U. Ladziata, V. V. Zhdankin, *Arkivoc* **2006**, *ix*, 26; e) V. V. Zhdankin, *Arkivoc* **2009**, *i*, 1-62.
- [2] For excellent monographs on hypervalent iodine chemistry, see: a) A. Vargolis, *Hypervalent Iodine in Organic Synthesis*, Academic Press, London, **1997**. b) *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis* (Ed.: T. Wirth), Topics in Current Chemistry, vol. 224, Springer, Berlin, **2003**. c) V. V. Zhdankin, *Hypervalent Iodine Chemistry*, John Wiley & Sons, Chichester, **2014**. d) b) *Hypervalent Iodine Chemistry* (Ed.: T. Wirth), Topics in Current Chemistry, vol. 373, Springer, Berlin, **2016**.
- [3] a) M. Brown, U. Farid, T. Wirth, *Synlett* **2013**, *24*, 424; b) R. M. Romero, T. H. Wöste, K. Muniz, *Chem. Asian J.* **2014**, *9*, 972; c) M. Fujita, *Tetrahedron Lett.* **2017**, *58*, 4409.
- [4] a) R. M. Moriarty, S. C. Gupta, H. Hu, D. R. Berenschot, K. B. White, *J. Am. Chem. Soc.* **1981**, *103*, 686; b) M. Ochiai, A. Nakanishi, T. Suefuji, *Org. Lett.* **2000**, *2*, 2923; c) K. M. McQuaid, T. R. R. Pettus, *Synlett* **2004**, 2403; d) S. Lee, D. W. C. McMillan, *Tetrahedron* **2006**, *62*, 11413.
- [5] a) Y. N. Ito, T. Katsuki, "Oxidation of the C=C bond" in *Asymmetric Oxidation Reactions*, (Ed.: T. Katsuki), Oxford University Press, **2001**, ch. 2.1, pp. 19-37. b) T. Katsuki, *Synlett* **2003**, 281.
- [6] For excellent overviews, see: a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*, Wiley, New York, **1998**; b) H. M. L. Davies, E. G. Antoulinakis, *Org. React.* **2001**, *57*, 1; c) M. P. Doyle, T. Ren, K. D. Karlin, *Prog. Inorg. Chem.* **2001**, *49*, 113; d) C. A. Merlic, A. L. Zechman, *Synthesis* **2003**, 1137; e) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861; f) A. G. H. Wee, *Curr. Org. Synth.* **2006**, *3*, 499; g) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417; h) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704; i) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, M. A. McKervey, *Chem. Rev.* **2015**, *115*, 9981.
- [7] S. P. Uemura, S. R. Patil, *Chem. Lett.* **1982**, 1743.
- [8] a) A. J. Catino, R. E. Forslund, M. P. Doyle, *J. Am. Chem. Soc.* **2004**, *126*, 13622; b) A. J. Catino, J. M. Nichols, H. Choi, S. Gottipamula, M. P. Doyle, *Org. Lett.* **2005**, *7*, 5167; c) E. C. McLaughlin, H. Choi, K. Wang, G. Chiou, M. P. Doyle, *J. Org. Chem.* **2009**, *74*, 730; d) M. O. Ratnikov, M. P. Doyle, *Mendeleev Comm.* **2014**, *24*, 187; e) J. A. S. Coelho, A. F. Trindade, R. Wanke, B. G. M. Rocha, L. F. Veiros, P. M. P. Gois, A. J. L. Pombeiro, C. A. M. Afonso, *Eur. J. Org. Chem.* **2013**, 1471; f) Y. Wang, Y. Kuang, Y. Wang, *Chem. Commun.* **2015**, 51, 5852; g) L. Zhao, Y. Wang, Z. Ma, Y. Wang, *Inorg. Chem.* **2017**, *56*, 8166; h) Y. Lin, L. Zhu, Y. Lan, Y. Rao, *Chem. Eur. J.* **2015**, *21*, 14937.
- [9] D. Shabashov, M. P. Doyle, *Tetrahedron* **2013**, *69*, 10009.
- [10] For reviews, see a) P. Müller, *Acc. Chem. Res.* **2004**, *37*, 243; b) M. S. Yusubov, A. Yoshimura, V. V. Zhdankin, *Arkivoc* **2016**, *i*, 342. For some relevant examples, see: c) P. Müller, D. Fernandez, *Helv. Chim. Acta* **1995**, *78*, 947; d) R. P. Wurz, A. B. Charette, *Org. Lett.* **2003**, *5*, 2327; e) S. R. Goudreau, D. Marcoux, A. B. Charette, D. Hughes, *Org. Synth.* **2010**, *87*, 115; f) S. A. Wolckenhauer, A. S. Devlin, J. Du Bois, *Org. Lett.* **2007**, *9*, 4363; g) C. Zhu, A. Yoshimura, L. Ji, Y. Wei, V. N. Nemykin, V. V. Zhdankin, *Org. Lett.* **2012**, *14*, 3170.
- [11] For reviews, see: a) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905; b) P. Dauban, R. H. Dodd, *Synlett* **2003**, 1571; c) J. W. W. Chang, T. M. U. Ton, P. W. H. Chan, *Chem. Rec.* **2011**, *11*, 331; d) J. Du Bois, *Org. Process. Res. Dev.* **2011**, *15*, 758; e) J. L. Roizen, M. E. Harvey, J. Du Bois, *Acc. Chem. Res.* **2012**, *45*, 911; f) D. Karila, R. H. Dodd, *Curr. Org. Chem.* **2011**, *15*, 1507; g) G. Dequerez, V. Pons, P. Dauban, *Angew. Chem.* **2012**, *124*, 7498; *Angew. Chem. Int. Ed.* **2012**, *51*, 7384; h) J. Buendia, G. Grelier, P. Dauban, *Adv. Organomet. Chem.* **2015**, *64*, 77.
- [12] For relevant studies, see: a) R. Breslow, S. H. Gellman, *J. Am. Chem. Soc.* **1983**, *105*, 6728. b) P. Müller, C. Baud, Y. Jacquier, *Tetrahedron* **1996**, *52*, 1543; c) I. Nägeli, C. Baud, G. Bernardinelli, Y. Jacquier, M. Moran, P. Müller, *Helv. Chim. Acta* **1997**, *80*, 1087; d) C. G. Espino, J. Du Bois, *Angew. Chem.* **2001**, *113*, 618; *Angew. Chem. Int. Ed.* **2001**, *40*, 598; e) C. G. Espino, P. M. Wehn, J. Chow, J. Du Bois, *J. Am. Chem. Soc.* **2001**, *123*, 6935; f) K. Guthikonda, J. Du Bois, *J. Am. Chem. Soc.* **2002**, *124*, 13672; g) K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.* **2007**, *129*, 562; h) R. H. Perry, T. J. Cahill III, J. L. Roizen, J. Du Bois, R. N. Zare, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 18295; i) J. L. Roizen, D. N. Zalatan, J. Du Bois, *Angew. Chem.* **2013**, *125*, 11553; *Angew. Chem. Int. Ed.* **2013**, *52*, 11343; j) M. Anada, M. Tanaka, N. Shimada, H. Nambu, M. Yamawaki, S. Hashimoto, *Tetrahedron* **2009**, *65*, 3069; k) A. Nörder, S. A. Warren, E. Herdtweck, S. M. Huber, T. Bach, *J. Am. Chem. Soc.* **2012**, *134*, 13524; l) C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd, P. Dauban, *J. Am. Chem. Soc.* **2008**, *130*, 343; m) J. Ciesielski, G. Dequerez, P. Retailleau, V. Gandon, P. Dauban, *Chem. Eur. J.* **2016**, *22*, 9338; n) J. Buendia, B. Darses, P. Dauban, *Angew. Chem.* **2015**, *127*, 5789; *Angew. Chem. Int. Ed.* **2015**, *54*, 5697; o) J. Buendia, G. Grelier, B. Darses, A. G. Jarvis, F. Taran, P. Dauban, *Angew. Chem.* **2016**, *128*, 7656; *Angew. Chem. Int. Ed.* **2016**, *55*, 7530.
- [13] a) B. Darses, R. Rodrigues, L. Neuville, M. Mazurais, P. Dauban, *Chem. Commun.* **2017**, 53, 493; b) D. Hazeldar, P.-A. Nocquet, P. Compain, *Org. Chem. Front.* **2017**, *4*, 2500.
- [14] C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.* **2004**, *126*, 15378.
- [15] D. Clemente-Tejeda, A. Lopez-Moreno, F. A. Bernejo, *Tetrahedron* **2013**, *69*, 2977.
- [16] Though the difference in yields between the entries 12 and 13 is not significant, the choice of PhI(OPiv)₂ as the oxidant to study the scope of the reaction was motivated by the reaction of alkene **1i** with PhI(OAc)₂ that leads to the expected epoxide **2i** in only 40% yield (70% with PhI(OPiv)₂; see table 2).
- [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.
- [20] It is worth mentioning that the reaction of *m*-CPBA with the *ortho*-cyano styrene only leads to the corresponding epoxide **2s** in 13% yield. See: "ACC inhibitors and uses thereof", PCT/ WO 2013071169A1, May 16, 2013.
- [21] K. Miyamoto, N. Tada, M. Ochiai, *J. Am. Chem. Soc.* **2007**, *129*, 2772.
- [22] Use of other Lewis acids such as Cu(OTf)₂, Pd(OAc)₂, BF₃·OEt₂, Sc(OTf)₃, CeCl₃, LiCl, or TMSOTf, in the epoxidation of **1i** leads to either its decomposition or the formation of the expected product **2i** in very low yield.
- [23] For a previous Lewis acid-catalyzed olefin epoxidation with an iodine(III) oxidant, see: Y. Yang, F. Diederich, J. S. Valentine, *J. Am. Chem. Soc.* **1991**, *113*, 7195.
- [24] The electron-withdrawing property of the ligand on the dirhodium complex would allow for tuning its Lewis acidity. The latter should be Lewis acidic enough for the activation of the hypervalent iodine reagent, however, a too strong Lewis acid is likely to increase its oxidizing character thereby inducing the decomposition of the resulting epoxide, as demonstrated by the study of Ochiai (see ref. 21).
- [25] It should be mentioned that a recent theoretical study supports a metathesis mechanism for the functionalization of alkenes using a hypervalent fluoriodine reagent. J. Zhang, K. J. Szabo, F. Himoto, *ACS Catal.* **2017**, *7*, 1093.
- [26] P. Šiška, D. Danková, C. Nitrayová, P. Fodran, I. Špánik, P. Szolcsányi, *Synth. Commun.* **2017**, *47*, 1582.
- [27] A. Méou, M. A. Garcia, P. Brun, *J. Mol. Catal. A Chem.* **1999**, *138*, 221.
- [28] O. P. Vig, I. R. Trehan, G. L. Kad, J. Ghose *Indian J. Chem.* **1983**, *22B*, 515.
- [29] H. Steinmetz, J. Li, C. Fu, N. Zaburannyi, B. Kunze, K. Harmrolfs, V. Schmitt, J. Herrmann, H. Reichenbach, G. Höfle, M. Kalesse, R. Müller, *Angew. Chem. Int. Ed.* **2016**, *55*, 10113.
- [30] Y. H. Kim, B. C. Chung, *J. Org. Chem.* **1983**, *48*, 1562.
- [31] A. Mordini, D. Peruzzi, F. Russo, M. Valacchi, G. Reginato, A. Brandi, *Tetrahedron* **2005**, *61*, 3349.
- [32] T. J. Harrison, P. M. A. Rabbat, J. L. Leighton, *Org. Lett.* **2012**, *14*, 4890.
- [33] J. Tsuji, H. Kataoka, Y. Kobayashi, *Tetrahedron Lett.* **1981**, *22*, 2575.
- [34] Z.-X. Wang, Y. Tu, M. Frohn, J.-R. Zhang, Y. Shi, *J. Am. Chem. Soc.* **1997**, *119*, 11224.
- [35] L. A. Flippin, P. A. Brown, K. Jalali-Araghi, *J. Org. Chem.* **1989**, *54*, 3588.
- [36] T. Mukaiyama, K. Imagawa, T. Yamada, T. Takai, *Chem. Lett.* **1992**, *21*, 231.
- [37] S. Pedragosa-Moreau, C. Morisseau, J. Zylber, A. Archelas, J. Baratti, R. Furstoss, *J. Org. Chem.* **1996**, *61*, 7402.
- [38] S. Qian, T. He, W. Wang, Y. He, M. Zhang, L. Yang, G. Li, Z. Wang, *Bioorg. Med. Chem.* **2016**, *24*, 6194.

Entry for the Table of Contents (Please choose one layout)

FULL PAPER

**Alkene epoxidation***

*Ali Nasrallah, Gwendal Grelier, Maria Ivana Lapuh, Fernando J. Duran, Benjamin Darses, Philippe Dauban**

Page No. – Page No.

Dirhodium(II)-mediated alkene epoxidation with iodine(III) oxidants

Switch O-N. 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 would involve a Lewis acidic dirhodium(II) complex bound to an iodonium species that would undergo nucleophilic displacement with water.