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Oxygen transfer reactions from an Oxaziridinium tetrafluoroborate salt to Olefins

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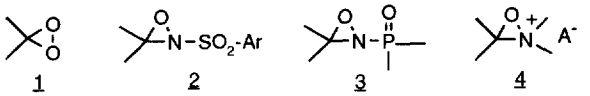
Abstract: Oxaziridinium 5 efficiently epoxidises olefins. It reacts as an electrophilic reagent and does not transfer its oxygen to deactivated double-bonds or carbonyl functions. Epoxidation of cyclic allylic acetates shows a remarkable diastereoselectivity leading to the syn isomer. We propose that the epoxidation reaction proceeds through a one-step process. © 1997 Elsevier Science Ltd.

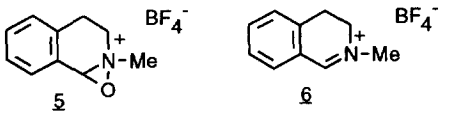
Dioxiranes [1] 1, N-sulfonyloxaziridines [2] 2, and N-phosphonyloxaziridines [3] 3 are oxygen transfer reagents which can perform epoxidation reactions.



1 2 3 4

The oxaziridinium function [4] 4 exhibits similar properties. Preliminary results have shown that oxygen transfer reactions onto olefins take place using either an isolated oxaziridinium salt 5, or one prepared *in situ* by peracidic oxidation of the corresponding iminium salt 6 [5]. Using the latter strategy, a catalytic cycle has been developed [6].

The stereospecificity of the epoxidation process and the influence of neighbouring functionalities to the double-bond have been examined and the results are reported herein.



5 6

Results:

In dichloromethane, oxaziridinium salt 5 efficiently transfers oxygen to unfunctionalised double-bonds, as shown in Table 1. Like peracids, oxaziridinium salt 5 effects oxygen transfer in a stereospecific manner. Under identical conditions, the reaction time is shorter with oxaziridinium salt 5 compared to *meta*-chloroperbenzoic acid. The oxygen transfer can also be performed with *m*CPBA in the presence of a substoichiometric amount of

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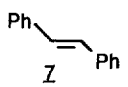
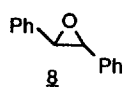
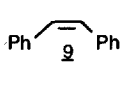
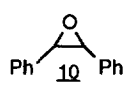
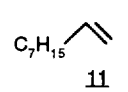
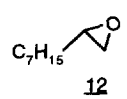
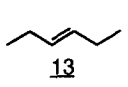
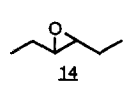
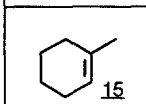
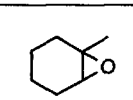
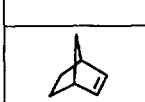
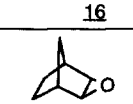
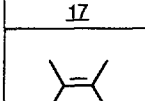
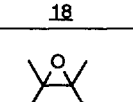
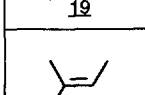
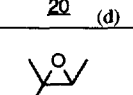
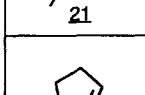
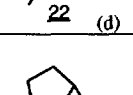
Table 1

Epoxidation of Unfunctionalised Double-bonds by Oxaziridinium salt 5 *versus meta*-Chloroperbenzoic acid (e).

Substrate (a)	Oxaziridinium 5 Time (b)	Yield (c)	*m*CPBA Time(b)	Yield(c)	Product	Reference
 7	30 mn	96%	4 hours	95%	 8	[7]
 9	1 hour	89%	3 hours	92%	 10	[8]
 11	2 hours	91%	10 hours	88%	 12	[9]
 13	1 hour	85%	2 hours	92%	 14	[10]
 15	10 mn	84%	1 hour	88%	 16	[11]
 17	10 mn	75%	40 mn	70%	 18	[12]
 19	< 5 mn		5 mn		 20 (d)	[13]
 21	5 mn		10 mn		 22 (d)	[14]
 23	20 mn		30 mn		 24 (d)	[7]

a) Reaction conducted in dichloromethane at 200 mmol/L. b) Time required for active oxygen to disappear from the reaction mixture determined by IK test. The conversion ratio is determined by ^{1}H NMR examination. c) Isolated yields. d) Non isolated products. Conversion ratio higher than 95%. e) The isolated oxaziridinium salt 5 prepared by methylation of the corresponding oxaziridine has to be carefully neutralised or employed in the presence of sodium hydrogencarbonate. A solution of the oxaziridinium salt 5 prepared from peracid oxidation of the corresponding iminium salt 6 in the presence of 0.1 eq. of hydrogencarbonate may also be used.

the iminium salt 6. The average reaction times for this transfer are reported in Table 2.

Table 2

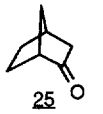
Epoxidation of three unfunctionnalised olefins by *meta*-chloroperbenzoic acid alone (A), *meta*-chloroperbenzoic acid with iminium salt 6 (10%) (B), and oxaziridinium salt 5 alone (C).

Substrate (a)	Reaction time (b)		
	A	B	C
trans-Stilbene 7	20 h	7 h (c)	3 h
cis-Stilbene 9	30 h	10 h (c)	6 h
Nonene-1 11	10 h	9 h (c)	8 h

a) Reaction conducted in dichloromethane at 50 mmol/L. b) Time required for active oxygen to disappear from the reaction mixture determined by IK test. Conversion ratio is higher than 95% as determined by ^{1}HNMR. c) Yields of isolated epoxides: from 7: 95%; from 9: 92%; from 11: 85%.

The above results show that Oxaziridinum salt 5 epoxidises *trans*-stilbene more efficiently than it oxidises *cis*-stilbene (Table 2, entry C). However, the time required to oxidise these two substrates with *m*CPBA is relatively similar (Table 2, entry A). To confirm these observations, two competitive reactions were completed. An equimolar mixture of the two substrates (7 and 9) was reacted with 0.2 equivalents of either salt 5 or *m*CPBA. A mixture of *cis/trans* epoxides was obtained in a 1/3 ratio for oxaziridinium salt 5 and a 1/1 ratio when *m*CPBA was used.

Peracids react with norbornanone 25 as nucleophiles in a Bayer-Villiger reaction [15,16] leading to lactone 26. On the other hand, Oxaziridinium salt 5 reacts only as an electrophile and does not transfer oxygen to the ketone 25.



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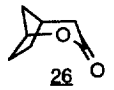

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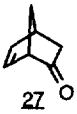
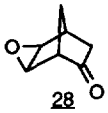
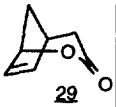
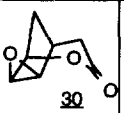
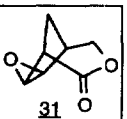
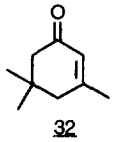
Hence, it should be possible to specifically epoxidise an olefin in the presence of a carbonyl using oxaziridinium salt 5. This was demonstrated using norbornenone 27 which was oxidised chemo and stereospecifically to the epoxyketone 28 in 86% yield using one equivalent of oxaziridinium 5 in the presence of sodium hydrogencarbonate (Table 3, entry 1). Such selectivity, which is also observed using dimethyldioxirane, (Table 3, entry 5) does not occur with a peracid (Table 3, entry 2) [17, 18]. It has been previously shown that peracetic acid primarily reacts with norbornenone 27 *via* a nucleophilic pathway leading to the γ-lactone 29 which then rearranges to a δ-lactone [17,18]. We observed that *m*CPBA reacts largely *via* an electrophilic pathway leading to the epoxyketone 28 (Table 3, entry 2). However, 28 partially reacts *in situ* to give a mixture of epoxylactones 30 and 31. When the reaction is conducted in the presence of one equivalent of $NaHCO_3$, the yield of epoxylactone 30 relative to epoxyketone 28 is increased (Table 3, entry 3). In the presence of 10% iminium salt 6 and one equivalent of $NaHCO_3$, the major product is epoxyketone 28 (Table 3, entry 4).

Table 3
Oxygen transfer reactions to norbornenone 27

Entry	Reagents	Conditions	 27	 28	 29	 30	 31
1	5 1 eq.	CH_2Cl_2 (c) $NaHCO_3$ 1 eq.		86% (a)			
2	*m*CPBA 1.1eq	$CDCl_3$ (b)	5%	60%	5%	25%	5%
3	*m*CPBA 1.1eq	$CDCl_3$ (b) $NaHCO_3$ 1 eq.	20%	25%	20%	25%	10%
4	*m*CPBA 1.1eq 6 0.1 eq.	$CDCl_3$ (b) $NaHCO_3$ 0.1 eq.	10%	85%		5%	
5	DMDO (d)	CH_3COCH_3		90% (a)			

a) Quantitative conversion. Isolated yield. b) Ratio in the crude mixture was determined by ^1H NMR (error ± 5% of the stated values). c) In the absence of sodium hydrogencarbonate the oxaziridnium salt 5 quantitatively gives the epoxide 28 which rearranges *in situ* to the δ-lactone reported in ref. [17, 18] (see experimental section). d) Dimethyldioxirane.

α,β-Unsaturated ketones such as isophorone 32 or cholestenone 33 are not transformed in the presence of oxaziridinium salt 5. However, under the reaction conditions, salt 5 is deoxygenated to the iminium salt 6. Oxaziridinium salt 5 epoxidises mesityl oxide 34. However, only 50% conversion is observed, although the reagent becomes totally deoxygenated. The double bond in the 4,5 position of ethyl sorbate 35 can be selectively epoxidised using two equivalents of oxaziridinium salt 5.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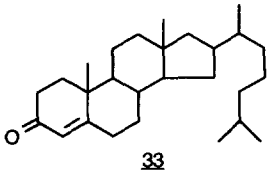
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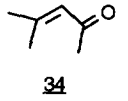
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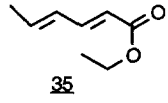
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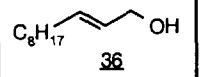
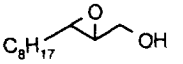
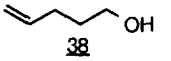
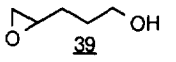
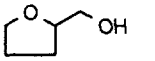
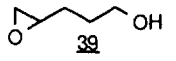
Morever, we observed that methyl-maleate and methyl-fumarate do not react with oxaziridinium salt 5 and that no deoxygenation reaction could be observed in these cases.

Two unsaturated alcohols 36 and 38 have been epoxidised in good yields using oxaziridinium salt 5. The results along with those obtained using *m*CPBA are listed in Table 4. It should be noted that oxidation of the 4-pentene-1-ol 38 gave tetrahydrofurfurylic alcohol 40 even when a neutralised oxaziridinium salt 5 was used (entry 4). Epoxide 39 was obtained either in the presence of sodium hydrogencarbonate (entry 5), or when the

oxaziridinium salt was prepared from peracid oxidation of the corresponding iminium salt [4] (see note (e) in Table 1).

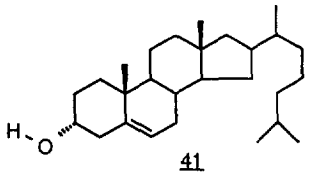
Table 4

Oxygen transfer reactions to unsaturated alcohols

Substrate	Entry	Reagents (a)	Products	Yields (b)	Reaction time
 36	1	*m*CPBA	 37	92%	7 hours
	2	5 (c)	37	95%	3 hours
 38	3	*m*CPBA	 39	86%	8 hours
	4	5 (c)	 40	95%	3.5 hours
	5	5 + $NaHCO_3$, 1eq. (c)	 39	88% (d)	3 hours

a) Reaction conducted in dichloromethane. b) Isolated yields. c) Neutralised on alcalin alumina. d) The same result is obtained when oxaziridinium salt 5 is prepared by peracid oxidation of iminium salt 6 in the presence of 0.1 eq. of sodium hydrogencarbonate and used without isolation.

As described for Dimethyldioxirane [19], Oxaziridinium salt 5 exhibits slight stereoselectivity for the epoxidation of cholesterol 41 and cholesterol acetate 42.



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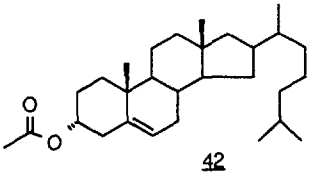

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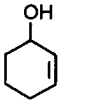
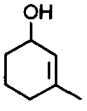
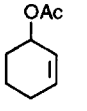
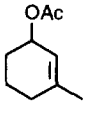
The ratio of α-epoxide/β-epoxide changes from 6/4 for 41 to 4/6 for 42. With *m*CPBA, we observed a ratio of 9/1 for 41 and 2/8 for 42. These results are in agreement with those described in the literature [20] for peracids.

It is well known that peracids epoxidise allylic alcohols *syn* to the hydroxyl group of the substrate [21a]. The same stereoselectivity has been described for allylic carbamates [21b]. Recently, W. Adam and R.W. Murray showed a hydroxy-directing effect in the oxidation of allylic alcohols with solvent dependence, using Dimethyldioxirane [22]. The epoxidation of two allylic cyclohexenols 43 and 44, and their corresponding acetates 45 and 46 with oxaziridinium salt 5 has also been studied. The stereospecificity of these reactions was compared to those observed when *m*CPBA or dimethyldioxirane were used (Table 5).

The *syn*-stereospecificity induced by the hydroxyl group which is observed when using a peracid or Dimethyldioxirane is not observed with the oxaziridinium salt 5. No C-H insertion on the hydroxyl function is

Table 5
Epoxidation of 2-cyclohexene-1-ol and 3-methyl-2-cyclohexene-1-ol and their corresponding acetates

Substrate	Reagent (a)	Reaction time (b)	Yield (c)	Ratio *syn/anti* (d)
 43	*m*CPBA	5 hours	98%	9.2/0.8
	Dimethyldioxirane	4 hours (e)	80%	47 7.5/2.5
	Oxaziridinium 5	3.5 hours	85%	6/4
 44	*m*CPBA	4.5 hours	95%	9.5/0.5
	Dimethyldioxirane	3 hours (e)	88%	48 7/3
	Oxaziridinium 5	3 hours	95%	6/4
 45	*m*CPBA	8 hours	90%	1/1
	Dimethyldioxirane	2 hours	95%	49 3.5/6.5
	Oxaziridinium 5	3 hours	92%	>9.5/0.5 (f, g)
 46	*m*CPBA	7 hours	95%	4/6
	Dimethyldioxirane	1.5 hours	90%	50 1/9
	Oxaziridinium 5	3 hours	95%	9.5/0.5 (f, g)

a) Reactions conducted in dichloromethane at 100 mmol/L. Acetone (10%) is used as a co-solvent when reactions are conducted with dimethyldioxirane. b) Time required to observe a negative IK test. c) Isolated yields of mixtures of *syn-anti* epoxides. d) The ratio *syn/anti* is determined by ^{1}H NMR in the presence of an internal reference (error ± 5% of the stated values). e) ^{1}H NMR analysis indicates the presence of 10% corresponding enone. f) If the reaction is performed in the presence of sodium hydrogencarbonate or in a mixture 8/2 dioxane/acetone, the ratio *syn/anti* reaches 1/1.

observed with oxaziridinium salt 5 as described and observed with dimethyldioxirane [25b]. However, the ester group induces a *syn*-stereospecificity using the oxaziridinium salt which is not observed in the case of the peracid. Dimethyldioxirane gives a moderate to good *anti*-stereospecificity with cyclohexenyl-acetates.

Discussion:

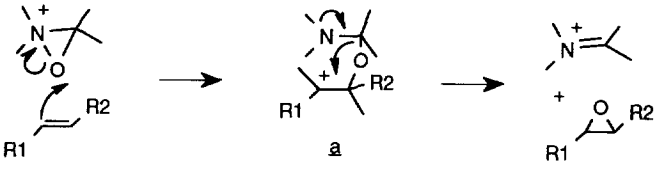
In the same manner as sulfonyloxaziridines and dioxiranes, oxaziridinium salt 5 is an electrophilic oxygen transfer reagent, which can be used as an epoxidation reagent. The electrophilic properties give short olefin epoxidation times which decreases as the olefins become increasingly nucleophilic (Table 1). Oxygen transfer is not observed with highly deactivated olefins such as ethyl maleate or fumarate.
Oxaziridinium salt 5, used in excess, epoxidises mesityl oxide 34 or ethyl sorbate 35 but does not present any oxygen transfer towards isophorone 32 and cholestenone 33. In contrast to dimethyldioxirane [23a, b], oxaziridinium salt 5 is not the reagent of choice for the epoxidation of α,β-unsaturated ketones. On the other hand, oxaziridinium salt 5 is quantitatively deoxygenated in the presence of the α,β-unsaturated substrates 32 and 33 leading to the iminium salt 6, leaving the olefins unchanged. Deoxygenation of an oxaziridinium salt by a substrate which remains unmodified has been observed with an N-oxide [23c]. The reaction in this case is

explained by an oxygen transfer onto the oxygen atom of the N-oxide followed by the loss of molecular oxygen leaving a tertiary amine which is rapidly oxygenated. However, such an explanation does not seem to be applicable to conjugated ketones.

Oxygen transfer, using a peracid in the presence of a substoichiometric amount of iminium salt 6, is largely achieved through oxaziridinium salt 5. However, the transfer can be directly performed using the peracid and 10% of iminium salt 6 as the result in table 3, entry 4 indicates (5% of lactone 30 is detected). It has been previously shown that generation of oxaziridinium salt 5 in a catalytic cycle can be best accomplished when the oxygen donor is oxone, since oxone cannot participate in the direct transfer of oxygen to the olefin [5].

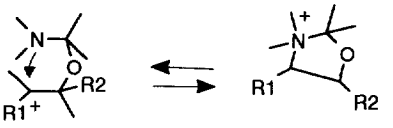
In contrast to peracids, oxaziridinium salt 5 is not nucleophilic and so does not react with the carbonyl function. This property, which has also been observed with sulfonyloxaziridines [2] and dioxiranes [1], allows the selective epoxidation of double-bonds in the presence of ketones. This was demonstrated for norbornenone 27 (Table 3). *m*CPBA reacts with 27 as a nucleophile and as an electrophile . The nucleophilic reaction can be enhanced in basic medium but the electrophilic reaction cannot be completely suppressed.

Oxygen transfer with salt 5 is stereospecific. *Cis* and *trans* olefins give the *cis* and *trans* epoxides respectively (Table 1). Such stereospecificity can be explained by a one-step oxygen transfer according to the interpretation generally given for peracids. Alternatively, this stereospecificity is compatible with a two-step oxygen-atom transfer (scheme 1), if the second step is faster than the C-C bond rotation at the carbocation center. However, the intermediate a could cyclise to give the oxazilidinium salt b.



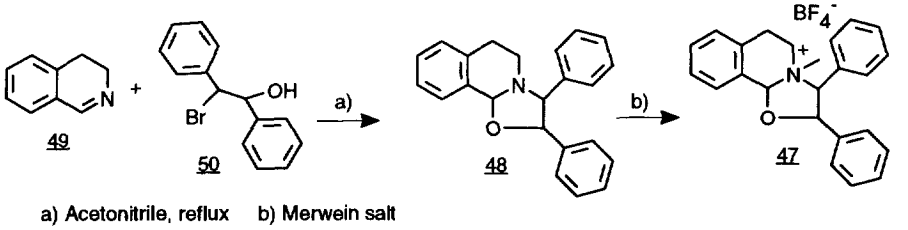
Scheme 1

In this case a two-step reaction could only be possible if the formation of the oxazilidinium salt b is reversible (Scheme 2).



Scheme 2

Some oxazilidinium salts have been reported in the literature [24]. The oxazilidinium salt 47 which could be formed during the epoxidation of *trans*-stilbene has been prepared from imine 49 (scheme 3).



a) Acetonitrile, reflux b) Merwein salt

Scheme 3

Oxazilidinium salt 47 was shown to be stable under the described epoxidation conditions. This result excludes a reversible cyclisation as denoted in scheme 2. A two-step oxygen-atom transfer appears to be unlikely and so a one-step mechanism with a transition state similar to the one described for peracids is proposed (figure 1).

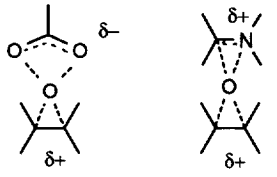


Figure 1

A peracid is neutral and the transition state of the epoxidation reaction is a dipole. In the case of the cationic oxaziridinium salt 5 , the positive charge is delocalised in the transition state. Therefore a partial positive charge remains on the nitrogen atom (figure 1). This rationale possibly explains the *syn*-selectivity observed for the epoxidation of substrates bearing a neighbouring acetate function (45 and 46) if the residual charge on the nitrogen atom and the carbonyl of the ester are able to associate themselves (figure 2) and (Table 5). In support of this hypothesis, we observed a decrease in the stereoselectivity when either a base was added to the reaction mixture or a basic polar solvent was used (Table 5, entry 3 and 4, f,g). No selectivity has been observed for homoallylic acetate 42 derived from cholesterol.
The *syn*-stereoselectivity induced by an hydroxyl group which is observed for peracids and under some conditions for dimethyldioxirane [25] is not observed with oxaziridinium salt 5.

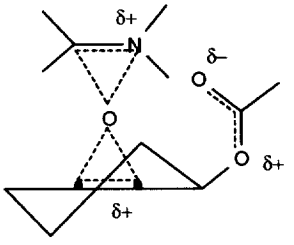


Figure 2

The strong electrophilic character of the oxygen in the oxaziridinium salt is not compatible with the formation of a hydrogen-bond with the allylic alcohol. Such hydrogen-bond interaction is the proposed explanation for the *syn*-stereoselectivity observed with a peracid [21] and with dimethyldioxirane [22]. With a protected hydroxyl group Dimethyldioxirane is known to give *anti*-stereoselectivity as a result of steric factors [25a]. The differences between the stereoselectivity of *m*CPBA, dimethyldioxirane and oxaziridinium salt 5 (Table 5) are significant and make these three reagents complementary in synthesis.

In conclusion, Oxaziridinium salt 5 can be used as an epoxidation reagent. The oxaziridinium function is related to electrophilic oxygen transfer reagents such as sulfonyloxaziridines or dioxiranes. These reagents exhibit different reactivities which can be of interest. The oxaziridinium salt 5 does not need to be isolated, but can be generated directly *in situ* by peracidic oxidation of the corresponding iminium salt 6. It can also be used in a catalytic cycle with oxone as the active oxygen donnor. In most of cases, very simple work up (precipitation) allows the isolation of the epoxides with recovery of the iminium salt 6 (see experimental). Finally, the results described reveal the significant and novel reactivity of an oxaziridinium salt towards olefins. Epoxidations of conformationally fixed cyclic allylic acetates and acyclic allylic acetates by oxaziridinium salt 5 are under investigations to try to define more precisely the transition state geometry. Further work is being conducted to identify other salts of interest and exploit their uses in synthesis.

Experimental Section:

General: All solvents were either *puriss p.a* or distilled over appropriate drying agents. TLC: *Merck-TLC-F_{254}* precoated glass plates, detection by UV_{254} light, staining with Draggendorf reagent, or with sulfuric acid and carbonisation. Chromatography: Silica gel *Merck 6H* (70-130 or 230-400 mesh) or neutral Alumina gel *Merck 90* (70-230 mesh ASTM). Melting point: *Leitz-Wetzler*, uncorrected. Mass Spectrometry: *AEI MS-50* (70 eV, EI), *MS-59* (CI), *MS-80* (FAB); in m/z (rel.intensities (%)). IR Spectra: *Perkin-Elmer-257* spectrometer in cm^{-1} in KBr disk or Chloroform soln.. UV spectra: *Perkin-Elmer Lambda 5 UV-Vis* absorption in nm and intensities in e. ^1H and ^{13}C NMR spectra: *Brüker VM200 and VM300* (200, 50 or 300, 75 MHz resp.); chemical shifts δ in ppm rel. to internal $SiMe_4$ for proton spectra or carbon signal of solvent for carbon spectra, coupling constant *J* in Hz. NMR ratio were determined from integration curves relative to internal references stable in the reaction conditions (diterbutylketone (δ: 1.18 ppm), stilbene-oxide (δ: 3.92 ppm) or dimethylsulfone (δ: 2.95 ppm). Elemental analysis: Microanalytical Laboratory of CNRS expressed in %. Commercially available *meta*-chloroperbenzoic acid was dried at room temperature at 5 torr and titrated by iodometric methodology.

Preparation of oxaziridinium salt 5: The oxaziridinium salt 5 was prepared from the corresponding oxaziridine as described in ref.[5]. We obtained a crystalline salt which was acidic (about pH 1). It can be neutralised by filtration through alcalin alumina and a crystallisation from acetone.

Preparation of a dichoromethane solution of oxaziridinium salt 5: A dichloromethane solution of oxaziridinium salt 5 can be prepared by peracid (*meta*-chloroperbenzoic or *para*-nitroperbenzoic acid) oxidation of the corresponding iminium salt 6 in the presence of 0.1 eq. of sodium hydrogencarbonate as described in ref.[5]. After filtration of the acid generated by the reaction, this solution may be used for oxygen transfer reactions.

General remarks about work up procedure of epoxidation reactions performed by oxaziridinium salt 5: Extraction of soluble epoxides in ethyl acetate could be accomplished *via* precipitation of the iminium salt 6 out of this solvent rather than washing the reaction mixture with water. The reaction mixture was concentrated *in vacuo* and the crude residue was stirred with ethyl acetate until the insoluble iminium salt 6 precipitated out of solution. After filtration, the organic solution was concentrated *in vacuo* to furnish epoxides and the solid was recrystalised from ethanol to give pure iminium salt 6 which may be used for an another oxygen transfer reaction.

General procedure for oxidations of olefins using *m*-CPBA: To a 5 mL stirred dichloromethane solution of olefin (0.1 mmol) was added in portions, 1.2 eq. (in active oxygen) of *m*-CPBA. The resulting reaction mixture was stirred until the peroxide test (IK) was negative. The precipitated acid was removed by filtration and the solution washed with saturated sodium hydrogencarbonate solution. Concentration *in vacuo* furnished the epoxide which was purified by flash-chromatography.

General procedure for oxidation of olefins using Dimethyldioxirane: To a stirred solution of olefin (0.1 mmol) in dichloromethane (8mL) was added a 0.05 M acetone solution of DMDO (2 mL). The solution was stirred at room temperature until the disappearance of active oxygen (IK test). The solvent was removed *in vacuo* to yield the corresponding epoxides.

Oxygen transfer reactions on unfunctionnalised Olefins using isolated oxaziridinium salt 5 (Table 1): -procedure for epoxidation yielding none volatile products (epoxides 8, 10, 12, 14, 16 and 18): A 5 mL dichlomethane solution of olefin (1 mmol) was stirred at room temperature with 1 eq. (249 mg) of oxaziridinium salt 5 until the disappearance of active oxygen (determined by IK test). An aliquot was sampled for NMR analysis(CD_3CN) to assess the conversion, which was higher than 95% (the proportion of the iminium salt 6 formed was identical to the epoxide). The reaction mixture was diluted with 10 mL of dichloromethane, washed 3 times with water to eliminate the iminium salt 6, dried over magnesium sulfate and concentrated *in vacuo*. The crude product was compared with the epoxide obtained from *m*CPBA oxidation, and had spectroscopic data consistent with reported values [7 to 14].

-reactions giving epoxides with low boiling points (epoxides 20, 22 and 24) were performed in sealed NMR tubes (using 0.8 mL of deuterated acetonitrile as solvent at 200 mmol/L) and followed by ^1H NMR until the disappearance of the oxaziridinium salt 5 (s at 6.2 ppm). The yield of non isolated epoxides was calculated with regard to internal reference (*trans*-stilbene oxide).

Oxygen transfer reactions on unfunctionnalised Olefins using oxaziridinium salt 5 prepared *in situ* (Table 2): To a 5 mL dichloromethane solution containing olefin (1 mmol), iminium salt 6 (0.1 eq., 23 mg) and $NaHCO_3$ (0.02 eq., 2 mg), *m*CPBA 202mg (1.05 eq. in active oxygen) was added at room temperature. The mixture was stirred until the

disappearance of active oxygen (determined by IK test), then washed with 3% $NaHCO_3$ solution and water before being dried and concentrated *in vacuo* to give *trans*-stilbene oxide 166 mg (85%), *cis*-stilbene oxide 180 mg (92%) and 1-nonene oxide 135 mg (95%).

Equimolecular mixture of *cis* and *trans* stilbene epoxidation; properties of oxaziridinium salt 5 versus *m*CPBA: Two 15 mL dichloromethane solutions containing a mixture of 0.15 mmol of *trans* Stilbene and *cis* Stilbene were prepared. Oxaziridinium salt 5 (0.06 mmol, 15 mg) was added to one and *m*CPBA (12 mg, O.2eq. of active oxygen) to the other. The reaction mixture was stirred until the disappearance of active oxygen (1 hour in the first case, 2 hours in the second one). The reaction mixture was washed with water and concentrated *in vacuo*, then dissolved in CD_3CN.^1H NMR analysis in the presence of diterbutylketone as internal reference gave a *cis/trans* ratio of 1/3 with oxaziridinium salt 5 and of 1/1 with *m*CPBA.

Preparation of 5-norbornenone 27: 5-norbornenone 27 was prepared according to the *Dess Martin* procedure [26], using periodinane and 5-norborneol (yield 75%). Spectroscopic data were consistent with reported values [27].

Oxygen transfer reactions on 5-norbornenone 27 (Table 3): reactions assayed by ^1H NMR were performed in $CDCl_3$ or CD_3CN (concentration 0.1M) in the presence of *trans*-stilbene oxide as internal reference.
Preparative scale reaction (Table 3, entry 1): To 10 mL of a dichloromethane solution containing 5-norbornenone 27 (108 mg, 1 mmol) and hydrogencarbonate (84 mg, 1 eq.), oxaziridinium salt 5 (249 mg, 1 eq.) was added in one portion. Stirring was continued until the disappearance of active oxygen (IK test). The reaction mixture was diluted with dichloromethane (10 mL) , washed with a 3% solution of $NaHCO_3$ and water before being concentrated *in vacuo*. Crystallisation of the residue from cold cyclohexane gave keto-epoxide 28 (107 mg, 86%) (Mp: 138°C, Lit: 138-140°C [28]) which had spectroscopic data consistent with that reported [28] and with a sample prepared by action of an acetone solution of dimethyldioxirane (13 mL at 0.075 M) on 1 mmol of 5-norbornenone 27.
When the same reaction was performed without sodium hydrogencarbonate, we obtained the pure δ-lactone in 88% yield [29] comming from isomerisation of keto-epoxyde 28 as reported in literature [17, 18]. The same product was obtained when pure epoxide 28 was stirred in dichloromethane in the presence of 0.05 eq. of trifluoroacetic acid.
The lactone 30 was isolated from crude product obtained by *m*CPBA oxidation of 5-norbornenone 27 (entry 2, Table 3), by flash chromatography using ethyl acetate/pentane; 1/1 as eluant. (Mp: 110°C, Lit: 107°C [17]). ^1H NMR (200 MHz, $CDCl_3$): 1.6 to 1.82 m (2H); 2.82 m (3H); 3.54 dd (1H, J= *4* and *6Hz*, Hep); 3.73 dd (1H, J= *4* and *6Hz*, Hep); 4.85 m (1H, J= 6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): 26.51 (CH_2); 30;842 (CH); 35.501 (CH_2CO); 52.241 (CHep.); 52.348 (CHep.); 53.921 CHCO); 178.008 (CO). MS(EI): for $C_7H_8O_3$: 140 $(M)^{+\cdot}$; IR ($CHCl_3$): 1730 cm^{-1} ($\nu_{C=O}$ δ-lactone); 1173 cm^{-1} and 840 cm^{-1}

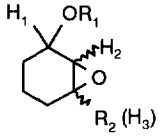
Ethyl sorbate 35 epoxydation: To a 5 mL dichloromethane solution containing ethyl sorbate 35 (140 mg, 1 mmol) was aded oxaziridinium salt 5 (498 mg, 2 eq.). The reaction mixture was stirred for 8 hours and then concentrated *in vacuo*. ^1H NMR analysis of the crude product in CD_3CN revealed a mixture of the corresponding epoxide and iminium salt 6. The crude mixture was diluted with 10 mL of dichloromethane, washed with water, dried over magnesium sulfate and concentrated *in vacuo*. The corresponding epoxide (132 mg, 85%) was obtained as a white solid and had spectroscopic data consistent with that of a sample prepared from *m*CPBA epoxidation and with values reported in the literature [30].

Unsaturated alcohols: oxygen transfer reactions (Table 4): 2-undecen-1-ol 36: The corresponding epoxide 37 was obtained (95% yield) following the above procedure (ethyl sorbate 35). The spectroscopic data was consistent with that of a sample prepared by the action of *m*CPBA on 36 and with reported values (Mp: 56-57°C, Lit: 58-59°C [31].
- 4-penten-1-ol 38: To 20mL of a dichloromethane solution containing olefin 38 (86 mg, 1 mmol) was added sodium hydrogencarbonate (84 mg, 1 eq.) and oxaziridinium salt 5 (249 mg, 1 eq.). The mixture was stirred at room temperature until the disappearance of active oxygen (IK test), diluted with 10 mL of dichloromethane, washed with water, dried over magnesium sulfate and concentrated *in vacuo*. The crude mixture was purified by chromatography over alcalin alumina using ether/pentane: 8/2 as eluent, to give epoxide 39 (81 mg, 88%) as an oil which was identical with a reference sample prepared by the action of *m*CPBA on 38 and had spectroscopic data consistent with reported values [32]. ^1H NMR (200 MHz, $CDCl_3$): 3.72 (2H, m , CH_2O); 3.03 (1H, m , CHO); 2.87 and 2.59 (2H, 2t , CH_2OH); 2.09 (1H, m , OH); 1.82 (2H, m); 1.70 (2H, m , CH_2).
In the absence of sodium hydrogencarbonate, the product was identified by comparison to a commercially available sample of tetrahydrofurfuryl alcohol 40. The epoxide 39 stirred in dichloromethane in the presence of 0.5 eq. of neutralised oxaziridinium salt 5 was isomerised to the alcohol 40.

Cholesterol derivatives 41 and 42 oxidation: To 20 mL of a dichloromethane solution containing cholesterol 41 (387 mg, 1mmol) was added oxaziridinium salt 5 (249 mg, 1 eq.). Upon disappearance of active oxygen (IK test) the reaction

mixture was concentrated *in vacuo*. The crude solid was stirred with ethyl acetate and insoluble iminium salt 6 precipitated out of solution. After filtration, the organic solution was concentrated *in vacuo* to give a mixture of diastereoisomers of cholesterol oxide in a ratio α/β: 6/4 (372 mg, 88%). The ratio was established by ^{1}H NMR integration of the signals corresponding to protons at the 6 position [33a]. Crystallisation from methanol gave 153 mg of α-epoxide which had spectroscopic data consistent with that of a sample prepared using *m*CPBA [33b]. Epoxidation of compound 42 (performed on 1 mmol) was conducted using exactly the same procedure and gave a ratio of α/β epoxides: 4/6. Crystallisation from methanol furnished 127 mg of pure β-epoxide which had spectroscopic data consistent with that of a sample prepared using *m*CPBA [33b].

Epoxidation of 2-cyclohexene-1-ol derivatives 43 44 45 46 (Table 5): All reactions were performed in 20 mL (or 7.5 mL for dimethyldioxirane) of dichloromethane on 1 mmol of substrate 43 to 46 using 1 eq. of active oxygen (200 mg for *m*CPBA, 12.5 mL of acetone solution for dimethyldioxirane (0.08M) and 249 mg for oxaziridinium salt 5). The reaction mixtures were stirred until the disappearance of active oxygen (IK test). The corresponding epoxides were isolated by washing with a 3% solution of $NaHCO_3$ for the *m*CPBA reaction, by precipitation out of the solution of iminium salt 6 in ethyl acetate followed by filtration for oxaziridinium salt 5 reaction and by concentrating *in vacuo* for dimethyldioxirane reactions. Dried crude products were analysed by ^{1}H NMR in $CDCl_3$ in the presence of an internal reference which revealed only a mixture of *syn* and *anti* diastereoisomers of epoxides. The *syn/anti* ratio was calculated by integration of H_1, H_2 and H_3 or Me signals.



47 (R_1=H; R_2=H)	*syn*: H_1: 4.01 (td, *J=5 and 2 Hz*); H_2: 3.35 (m); H_3: 3.35 (m); lit. [34]: (3.9; 3.22; 3.22)
	anti: H_1: 4.05 (m); H_2: 3.28 (dd, *J=5 and 3Hz*); H_3: 3.1 (m); lit. [34]: (4; 3.23; 3.02)
48 (R_1=H; R_2=Me)	*syn*: H_1: 4 (m); H_2: 3.2 (d, *J=1Hz*); R_2: 1.36 (s); lit. [34]: (3.9 to 4; 3; 1.31)
	anti: H_1: 4 (m); H_2: 2.92 (d, *J=4Hz*); R_2: 1.32 (s); lit. [34]: (3.7 to 4; 2.9; 1.3)
49 (R_1=Ac, R_2=H)	*syn*: H_1: 5.11 (m); H_2: 3.32 (br); H_3: 3.32 (br); lit. [34]: (5.1; 3.17; 3.17)
	anti: H_1: 5.02 (m); H_2: 3.24 (br); H_3: 3.08 (m); lit. [34]: (4.98; 3.17; 3.05)
50 (R_1=Ac; R_2=Me)	*syn*: H_1: 5.12 (m); H_2: 3.16 (d, *J=3Hz*); R_2: 2.07 (s)
	anti: H_1: 5.01 (m); H_2: 2.86 (d, *J=6Hz*); R_2: 2.09 (s)

The crude mixtures obtained from epoxidation of 43 and 44 were acetylated in pyridine with acetic anhydride. After work up and purification by chromatography using petroleum ether/ether;8/2 as eluent, diastereoisomeric mixtures were obtained which had ^{1}H NMR and ^{13}C NMR data consistant with those obtained by epoxidation of 45 and 46.

Synthesis of the oxazilidinium salt 47 (Scheme 3): The bromohydrin 50 was prepared from *trans*-stilbene following the procedure described in reference [35]. To a 50 mL acetonitrile solution containing bromhydrin 50 (1.18g, 5 mmol) was added imine 49 (0.655g, 5 mmol) [5]. The reaction mixture was heated under reflux for 16h and poured into a 6% hydrogencarbonate solution (100 mL). Six extractions with dichloromethane gave an oil which was purified by chromatography using dichloromethane/methanol gradient 10/0 to 7/3 as eluent to furnish pure oxazolidine 48 (790 mg, 48%) (diastereoisomeric mixture 9/1). The major diastereoisomer was identified to the diastereoisomer reported in the literature [36]. ^{1}H NMR (200 MHz, $CDCl_3$): 2.85 m (2H, CH_2); 3.12 m (2H, CH_2); 4.0 d (1H, CH AB syst. *J=7Hz*); 4.8 d (1H, CH AB syst. *J=7Hz*); 5.8 s (1H, H at position 1); from 7.1 to 7.4 m (14H, aromatics). The minor diastereoisomer has an AB system at 4.21 and 5.22 *J=5Hz* and H at position 1 is at 5.6 ppm. For the diastereoisomeric mixture: Mp: 102°C, Lit. 101-108°C [36]. MS(CI): 328 $[MH]^+$; 132 $[C_9H_9NH]^+$; 107 $[C_6H_5CH{=}OH]^+$

To a 10 mL dichloromethane suspension containing trimethyloxonium tetrafluoroborate (Merwein salt) (234 mg, 1.52 mmol.) cooled at 0°C under argon atmosphere was added dropwise 500 mg (1 eq.) of oxazilidinones 48 in 10 mL of dichloromethane. The mixture was stirred until complete dissolution of the Merwein salt, then concentrated to 1/3 of the original volume and stored overnight at -18°C. The precipitate was filtered to give 558 mg of a white solid. Two recrystallisations from ethanol gave the pure major diastereoisomer of 47 (372 mg, 57%) as white crystals. Mp: 259°C; For $C_{24}H_{24}NOBF_4$: C: 66.88 (67.15); H: 5.69 (5.64); N: 3.15 (3.26). MS(FAB): 342 $(M)^+$; 146 (Iminium salt 6 cation); ^{1}H NMR (250 MHz, CD_3CN): 2.65 s (3H, N-methyl); 3.35 m (2H, methylene at position 4); 3.76 and 4.19 2m (2H, methylene at position 3); 4.97 and 5.98 2d (2H, AB syst. *J=10Hz*); 6.04 s (1H, H at position 1); 7.38 to 7.82 m (14H, aromatics). ^{13}C NMR (75 MHz, CD_3CN): 25.497 (CH_2(4)); 44.672 (CH_3, N-methyl); 60.583 (CH_2(3)); 82.710 (CH(11)); 84.184 (CH(1)); 98.946 (CH(12)); 127.441 (CH(9)); 128.038 to 133.065 (CH and C aromatics).

The oxazilidinium salt 47 was stable in dichloromethane in the presence of iminium salt 6 with 1 eq. of *trans*-stilbene or sodium hydrogencarbonate or trifluoroacetic acid.

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