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Synthesis of Epoxy (Meth)acrylic Esters by Selective Epoxidation of Unsaturated (Meth)acrylic Esters using the System H_2O_2 - Na_2WO_4 under Phase Transfer Catalysis

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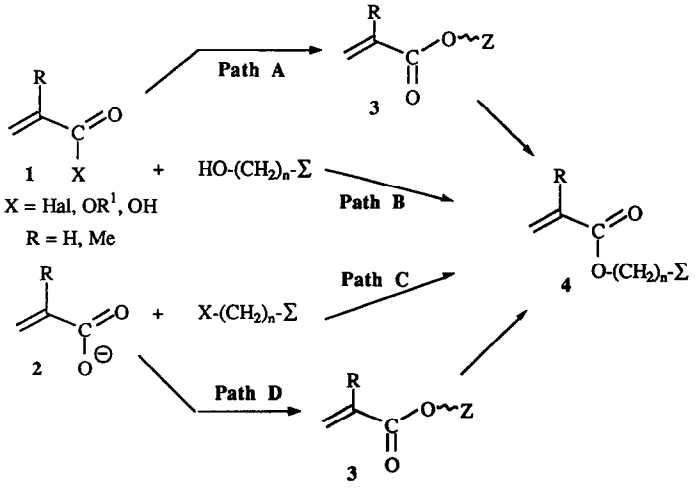
Abstract: Selective epoxidation of unsaturated (meth)acrylic esters by various classical epoxidizing agents was investigated. It is shown that high selectivity and good yields are obtained by using the system H_2O_2 (20%) - Na_2WO_4 under phase transfer catalysis. Under these conditions, the rigourous control of the temperature and of the initial pH allows to prevent polymerization during these selective epoxidations. It is shown that the selectivity of the epoxidation depends upon the difference of nucleophilicity of the two double bonds.

Functional (meth)acrylic monomers are the starting point of useful synthetic materials with widespread applications. Of course, the functional group anchored to the (meth)acrylic part must be tuned to the desired application. When the actival acrylic and (meth)acrylic characteristics, in other words the carbon-carbon unsaturation, unsubstituted or alpha-substituted by a methyl group, has to be strictly maintained, the functional group can only be introduced on the alkoxy part of the ester. Examination of the literature shows that this target may be reached thanks to the two types of reactions reported in Scheme 1.



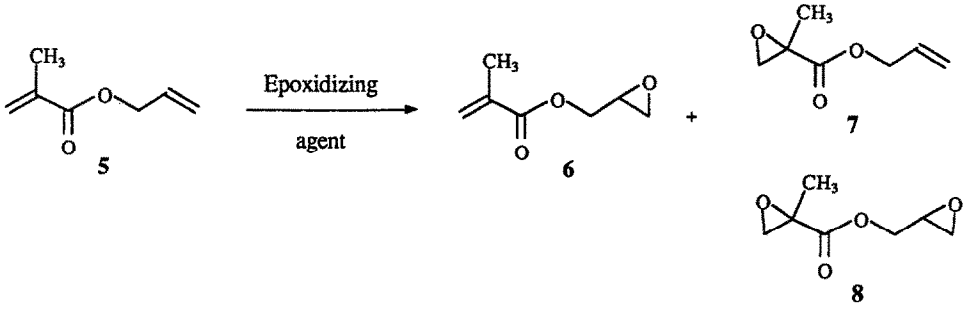
Scheme 1

The first kind of condensations (paths B and C), which includes esterifications and transesterifications, constitute a widespread method of synthesis of functional (meth)acrylic esters. However these syntheses suffer from a number of drawbacks particularly when the functional group Σ is sensitive to the experimental conditions. A two step reaction (paths A and D) where Z is a functional group tolerated during the condensation and easily transformed into Σ, would solve the problem. It must be emphasized that such an approach will also be of interest every time **3** is an easily available starting material.

As part of a program aiming at the synthesis of new acrylic and methacrylic monomers[1], we considered the second approach in order to synthesize epoxy derivatives starting from the corresponding unsaturated substrates. Taking into account the usual properties of carbon-carbon double bonds, it could be expected that the conjugated unsaturation would be less sensitive to electrophilic attack than the unconjugated one. However, a larger difference in reactivity in acrylic than in methacrylic series was expected. Indeed the electron donating property of the methyl group increases the electron density of the double bond. This effect has been recently confirmed.[2] In fact the present publication will show that selective oxidations do not follow such simple rules.

Results and Discussion

We decided to first study the selective epoxidation of 2-methyl-2-propenoic acid, vinyl methylester **5**, (commonly named allyl methacrylate or Maallyle) (scheme 2) for the following reasons : i) **5** is a very important industrial monomer prepared on a very large scale from allyl alcohol and methacrylic acid or epichorhydrin and methacrylate salt. ii) The corresponding monoepoxide **6** is also a very useful monomer with numerous important industrial applications.[3] iii) The structure of **5** is of particular interest as far as selective epoxidation is concerned. Indeed, as we mentioned *(vide supra)*, the electron-withdrawing effect of the carboalkenoxy group on the conjugated unsaturation is partially balanced by the electron donating effect of the methyl group. On the other hand, the weak electron-withdrawing effect of the oxygen on the unconjugated unsaturation slightly decrease the nucleophilicity of the double bond. The difference in reactivity of the two unsaturations against electrophilic reagents is the lowest we have found with this kind of monomer. Thus, it could be expected that any reagent able to selectively epoxidize **5** could be successfully used with other unsaturated methacrylates and acrylates.



Scheme 2

Exploratory experiments were performed in order to determine the behaviour of **5** against a number of oxidizing agents under standard unoptimized conditions. The results obtained are reported in Table 1.

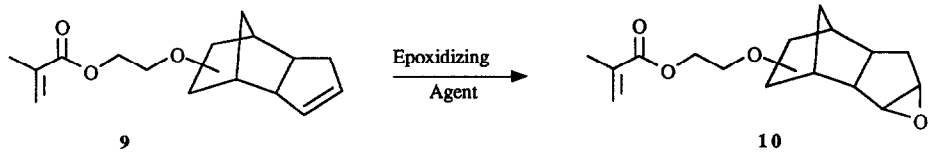
Table 1: Epoxidation of **5** with Usual Epoxidizing Agents.[a]

Entry	Oxidizing agent	Conditions[b]	Solvent	Temp. (°C)	time	Rec.5[c] (%)	yield (%)[c] 6	7	Lit. Ref.
1	Bu^tOOH-$Ti(OiPr)_4$	A	CH_2Cl_2	25	2 d	100	-	-	4
2	Bu^tOOH-$Mo(CO)_6$	B	C_6H_6	70	19 h	60	d	4[d]	5
3	Bu^tOOH-$VO(Acac)_2$	C	CH_2Cl_2	40	5 d	32	d	d	5,6
4	Bu^tOOH-$(ROBO)_3$	D	CH_2Cl_2	35	2 d	99	tr	-	7
5	$NaBO_3$-Ac_2O	E	CH_2Cl_2	35	2 d	100	-	-	8
6	MCPBA (55%)	F	$CHCl_3$	25	3 d	22	27[d]	14[d]	9
7	MMPP	G	$CHCl_3$	50	2 d	15	d	d	10
8	HCO_3H	H	$CHCl_3$	40	2 d	82	-	-	11
9	CH_3CO_3H	H	$CHCl_3$	40	2 d	12	d	15[d]	9
10	H_2O_2-CH_3CN	I	MeOH	25	4 d	1	d	d	12
11	H_2O_2 - Na_2WO_4	J	$C_2H_4Cl_2$	25	15 h	49	17	3	13
12	H_2O_2 - $C_{75}H_{162}N_3PW_4O_{24}$	K	$C_2H_4Cl_2$	25	96 h	95	2.2	0.5	14
13	H_2O_2 - $C_{50}H_{44}O_{11}P_2W_2$	L	$C_2H_4Cl_2$	25	96 h	98	tr.	tr.	15

[a] Reaction performed on a 50 mmoles scale. [b] Conditions and reagents. **A** : ButOOH 80 % (100 mmol), $Ti(OiPr)_4$ (2.5 mmol), MS4Å (2 g) in CH_2Cl_2 (100 ml) at 25 °C. **B** : ButOOH 70% (50 mmol), $Mo(CO)_6$ (3.5 mmol) in C_6H_6 at 7012 °C. **C** : ButOOH 70 % (75 mmol), $VO(acac)_2$ in CH_2Cl_2 (50 ml) at 40 °C. **D** : ButOOH 70 % (75 mmol), $(C_6H_{13}OBO)_3$ (2 mmol) in CH_2Cl_2 (50 ml) at 35 °C. **E** : $NaBO_3$ Ac2O (100 mmol) in CH_2Cl_2 (50 ml) at 35°C. **F** : MCPBA 55% (100 mmol) in $CHCl_3$ (50 ml) at 25 °C. **G** : MMPP (100 mmol) in $CHCl_3$ (50 ml) at 50 °C. **H** : HCO_3H or CH_3CO_3H (50 mmol) in $CHCl_3$ (50 ml) at 50 °C. **I** : H_2O_2 35 % (50 mmol), CH_3CN (100 mmol) in MeOH (15 ml) at 25 °C and pH = 8. **J** : H_2O_2 8 % (50 mmol), Na_2WO_4 (1.25 mmol), H_3PO_4 (2.1 mmol), Aliquat 336 (0.5 mmol) in $C_2H_4Cl_2$ (15 ml) at 25 °C and pH = 1.6. **K** : H_2O_2 30 % (80 mmol), $[W_2O_{11}{}^{2+},2\ Ph_3PCH_2{}^-]$ (0.5.mmol), in $C_2H_4Cl_2$ (50 ml) at 25 °C **L** : H_2O_2 16 % (15 mmol), $[C_8H_{17})NCH_3]^+{}_3[PO_4[W(O)(O_2)_2]_4]^{3-}$ (0.5.mmol) in $C_2H_4Cl_2$ (15 ml) at 25 °C [c] Yields determined by GC analysis. [d] Side reactions occured during these experiments.

From these data, there emerge a number of interesting points. We were never able to observe the formation of a diepoxide **8** due to the epoxidation of the two unsaturations. Curiously, a large number of usually very useful epoxidizing agents are completely inefficient with this substrate (entries 1,4,5). Note that the reactions must be performed under rather mild conditions in order to avoid polymerization of **5** as well as of **6** or **7**. Such side reactions happened with a number of oxidizing reagents (entries 2,3,6,7,9,10). As expected from the literature data, peracids[9-11] were the most efficient but their selectivity was rather low. Note that peracetic acid led to **7** as the only isolatable product. Moreover with peracids a number of side reactions took place and isolation of pure epoxides was often difficult. Finally, we have explored H_2O_2-Na_2WO_4 or H_2WO_4 under PTC conditions.[13,14,15] It appeared that conditions corresponding to run 11 were of the most practical interest.Side reactions were rather limited and the selectivity **6/7** was rather good. Moreover the reagent is unexpensive, easily prepared and may be easily used industrially. The only problem to solve was how to increase the yields.

Before devoting efforts to solve this last problem, we wanted to study the behaviour of a methacrylate monomer with more differentiated unsaturations. Moreover, being concerned with future industrial applications, we chose to work with compound **9** (Scheme 3).



9 10

Scheme 3

Actually the form under which **9** is industrially found is a mixture of isomers.[16] In such substrates the acrylic unsaturation is expected to be much less reactive against electrophilic agents than the unconjugated unsaturation. Indeed this latter is a disubstituted one and, above all, belongs to a very strained structure which considerably increases its reactivity. According to our expectations, exploratory experiments showed that epoxidation of the methacrylic unsaturation was never observed. The results obtained with a number of selected oxidizing agents are reported in Table 2.

Table 2. Epoxidation of **9** with usual epoxidizing agents.[a]

Entry	Oxidizing agent	Conditions[b]	Solvent	Temp. (°C)	time (h.)	Rec.**9** (%)[c]	yield **10** (%)[c]	Ref. Lit.
1	Bu^tOOH-$Ti(OiPr)_4$	A	CH_2Cl_2	25	18	95	tr.	4
2	Bu^tOOH-$Mo(CO)_6$	B	C_6H_6	70	4.5	40	56.5	5
3	Bu^tOOH-$VO(Acac)_2$	C	CH_2Cl_2	40	19	31	tr.	5,6
4	Bu^tOOH-$(ROBO)_3$	D	CH_2Cl_2	35	24	90	5	7
5	$NaBO_3$-Ac_2O	E	CH_2Cl_2	35	96	64	34	8
6	MCPBA (55%)	F	$CHCl_3$	25	1	-	99	9
7	MMPP	G	$CHCl_3$	50	18	46	53	10
8	HCO_3H	H	$CHCl_3$	40	8	8	92	11
9	CH_3CO_3H	H	$CHCl_3$	40	1	tr.	99	9
10	H_2O_2-CH_3CN	I	MeOH	25	4.5	89.5	11	12
11	H_2O_2 - Na_2WO_4	J	$C_2H_4Cl_2$	25	7	50	50	13

[a] Reaction performed on a 50 mmoles scale. [b] Conditions and reagents. **A** : Bu^tOOH 80 % (100 mmol), $Ti(OiPr)_4$ (2.5 mmol), MS4Å (2 g) in CH_2Cl_2 (100 ml) at 25 °C. **B** : Bu^tOOH 70% (50 mmol), $Mo(CO)_6$ (3.5 mmol) in C_6H_6 at 70 °C. **C** : Bu^tOOH 70 % (75 mmol), $VO(acac)_2$ (7 mmol) in CH_2Cl_2 (50 ml) at 40 °C. **D** : Bu^tOOH 70 % (75 mmol), $(C_6H_{13}OBO)_3$ (2 mmol) in CH_2Cl_2 (50 ml) at 35 °C. **E** : $NaBO_3$ 00 mmol), Ac_2O (100 mmol) in CH_2Cl_2 (50 ml) at 35°C. **F** : MCPBA 55% (100 mmol) in $CHCl_3$ (50 ml) at 25 °C. **G** : MMPP (100 mmol) in $CHCl_3$ (50 ml) at 50 °C. **H** : HCO_3H or CH_3CO_3H (50 mmol) in $CHCl_3$ (50 ml) at 50 °C. **I** : H_2O_2 35 % (50 mmol), CH_3CN (100 mmol) in MeOH (15 ml) at 25 °C and pH = 8. **J** : H_2O_2 8 % (50 mmol), Na_2WO_4 (1.25 mmol), H_3PO_4 (2.1 mmol), Aliquat 336 (0.5 mmol) in $C_2H_4Cl_2$ (15 ml) at 25 °C and pH = 1.6. [c] Yields determined by GC analysis.

The higher reactivity of the unconjugated unsaturation clearly appears from these data compared to those of Table 1. Peracids appeared as particularly well suited. However we encountered a number of difficulties during the isolation of **10** which was often obtained pure only in low yields. On the other hand the unexpensive H_2O_2-Na_2WO_4 appeared less efficient than peracids but isolation of **10** was easier. The above results encouraged us to improve the possibilities offered by H_2O_2-Na_2WO_4 under PTC conditions.

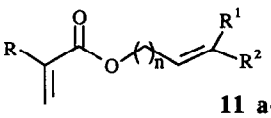
To do so we particularly came back to the very sensitive allyl methacrylate **5** and performed the reactions reported in Table 3 where a number of parameters of these reactions were studied.

Table 3. Exploratory experiments of the selective epoxidation of **5** and **9** with H_2O_2 - Na_2WO_4.[a]

Entry	Substrate	PTC catalyst	solvent	Temp. (°C)	initial pH[b]	[H2O2][c] (%)	time (h.)	Rec.[d](%) 5 or 9	yield (%)[d] 6 or 10	7
1	**5**	Aliquat 336	CH_2Cl_2	70	1.7	8	1.5		[e]	
2	**5**	Aliquat 336	CH_2Cl_2	40	1.7	8	45		[e]	
3	**5**	Aliquat 336	CH_2Cl_2	25	1.7	8	144	37	47.5	4
4	**5**	Aliquat 336	CH_2Cl_2	25	1.7	20	208	13	67	3
5	**5**	Aliquat 336	CH_2Cl_2	25	1.7	35	160	28	46.5	4
6	**5**	Aliquat 336	CH_2Cl_2	25	1.5	20	144	26	54.5	3
7	**5**	Aliquat 336	CH_2Cl_2	25	1.6	20	160	15	60.5	3
8	**5**	Aliquat 336	CH_2Cl_2	25	1.8	20	192	14	65	3
9	**5**	Aliquat 336	CH_2Cl_2	25	1.9	20	232	8	70	2.5
10	**5**	Aliquat 336	CH_2Cl_2	25	2.0	20	187	13	63	3
11	**5**	Bu_4NBr	CH_2Cl_2	25	1.7	20	144	77	9	<1
12	**5**	Bu_4PCl	CH_2Cl_2	25	1.7	20	168	70	18	1.5
13	**5**	Bu_4PBr	CH_2Cl_2	25	1.7	20	144	73	13	1.2
14	**5**	$Bu_3(C_{16}H_{31})PBr$	CH_2Cl_2	25	1.7	20	168	62	21.5	1.5
15	**9**	18K6	CH_2Cl_2	25	1.7	20	120	>95	-	-
16	**9**	Aliquat 336	CH_2Cl_2	25	1.7	20	5	2	98	-
17	**9**	Aliquat 336	$CHCl_3$	25	1.7	20	6	2	98	-
18	**9**	Aliquat 336	CCl_4	25	1.7	20	5	8.5	91.5	-
19	**9**	Aliquat 336	$C_2H_2Cl_2$	25	1.7	20	6	1	99	-
20	**9**	Aliquat 336	$C_5H_5CH_3$	25	1.7	20	5	4	96	-

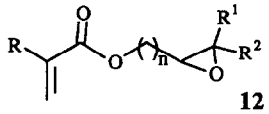
[a] Reaction performed on a 50 mmoles scale with H_2O_2 (100 mmol), Na_2WO_4 (1.25 mmol), H_3PO_4 (2.1 mmol), Aliquat 336 (1 mmol) in 15 ml of solvent. [b] Initial pH was ajusted at the right value with a 10% H_2SO_4 or a10 % NaOH solution. [c] Concentration of H_2O_2. [d] Yields determined by GC analysis by the internal standard method. [e] Polymerization occured during manipulation.

From these data it appears that Aliquat 336 (2 moles %) in chlorinated solvents such as methylene chloride or dichloroethane must be used. Methylen chloride is of particular interest since it may be easily removed under very mild conditions. The reaction temperature is a crucial point with allyl methacrylate **5** since many by-products were formed above 25°C. In fact with less sensitive monomers, a higher temperature may be used *(vide infra)*. Another important factor was the pH of the reaction medium which must be situated between 1.7 and 1.9. In fact, a low pH increases the efficiency of the oxidizing agent but favoured unwanted polymerizations simultaneously. Higher initial pH favored epoxide stabilization but lowered the epoxidation rate. Finally, the influence of H_2O_2 concentration was examined and it was found that H_2O_2 20 % in volume was the best. With these results in hand we were able to perform the epoxidation of various unsaturated (meth)acrylates (scheme 4) and the results were reported in Table 4.



11 a-m

a : R = R^1 = R^2 = H n = 1
b : R = Me R^1 = R^2 = H n = 2
c : R = R^1 = R^2 = H n = 2
d : R = Me R^1 = R^2 = H n = 4
e : R = R^1 = R^2 = H n = 4
f : R = Me R^1 = R^2 = H n = 8
g : R = R^1 = R^2 = H n = 8



12 a-m

h : R = R^1 = Me R^2 = H n = 1
i : R = R^2 = H R^1 = Me n = 1
j : R = R^1 = R^2 = Me n = 1
k : R = H R^1 = R^2 = Me n = 1
l : R = Me R^1 = H R^2 = Ph n = 1
m : R = R^1 = H R^2 = Ph n = 1

Scheme 4

Table 4. Epoxidation of Linear Unsaturated (Meth)Acrylic Esters with H_2O_2 -Na_2WO_4under PTC.[a]

Entry	Substrate	time (h.)	Product	Rec. **5** or **11** (%)[b]	Yield of **6** or**12** (%)[c]
1	**5**	208	**6**	13	50 (57)[d]
2	**5**	45	**6**	40	30 (49)
3	**11a**	188	**12a**	30	27 (38)[d]
4	**11a**	22	**12a**	10	[e]
5	**11b**	23	**12b**	19	52 (64)
6	**11c**	20	**12c**	15	60 (70)
7	**11d**	10	**12d**	24	50 (66)
8	**11e**	20	**12e**	9	65 (71)
9	**11f**	22	**12f**	23	66 (86)
10	**11g**	20	**12g**	10	68 (75)
11	**11h**	30	**12h**	17	70 (84)
12	**11i**	40	**12i**	3	74 (76)
13	**11j**	5	**12j**	3	70 (72)
14	**11k**	5	**12k**	4	60 (63)
15	**11l**	35	**12l**	23	57 (74)
16	**11m**	30	**12m**	31	50 (72)

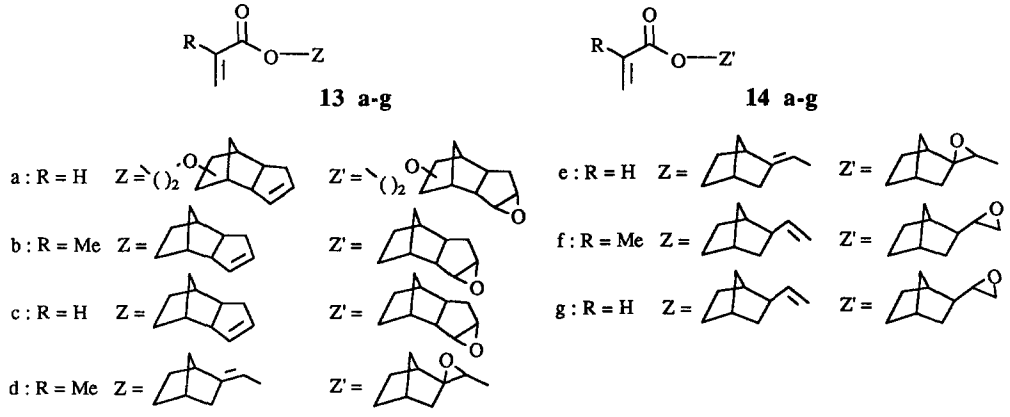
[a] Reaction performed on a 20 mmol scale at 40 °C (see experimental section). [b] Yield of recovered **5** or **11**. [c] Isolated yield by flash chromatography. In parenthesis, isolated yield based on converted **5** or **11**. [d] Reaction performed at 25 °C. [e] 17 % of **12a** was observed by GC analysis, polymerisation occured during isolation.

It appears that selective epoxidation of linear unsaturated (meth)acrylic esters may be easily performed and that epoxides may be isolated in fair to good yields. Note that about 10 to 15 % of the wanted epoxides unavoidably polymerize during the isolation of the monomers.

Moreover (meth)acrylic monomers appeared less sensitive to a temperature increase than **5**. Thus in order to shorte reaction times, the oxidations were performed at 40°C. During these epoxidations, a number of side reactions such as polymerizations of the starting material or hydrolysis and polymerization of the expected products may take place. On the other hand, more or less large amounts of stabilizing

agents have to be added during the reaction. Thus it is difficult to accurately discuss the above results. However some interesting tendencies emerge. Thus removing the unconjugated unsaturation from the oxygen of the ester function increases the nucleophilicity of the double bond and thus favors the epoxidation yields (compare for example entry 2 to entries 5, 7, 9). Comparison of runs 2 and 4 with 11, 13, 15 and 12, 14, 16 respectively shows that methyl as well as phenyl substituents on the unconjugated unsaturation also favor the selective epoxidations as expected from inductive and mesomeric carbocation stabilizing effects.

Thus from a practical point of view, it may be concluded that unsaturated (meth)acrylic monomers will be more selectively and easily epoxidized as the number of cationic stabilizing substituents increases. With unsubstituted double bonds, good results may be obtained as soon as at least two methylene groups separate the double bond from the oxygen of the ester function.The above results were extended to the industrial monomers (scheme 5) and the results were reported in Table 5.



Scheme 5

Table 5. Selective Epoxidation of Globular (Meth)Acrylic Esters with H_2O_2-Na_2WO_4under PTC.[a]

Entry	Substrate	time (h.)	Product	yield (%)[b]
1	**9**	10	**10**	95
2	**13a**	10	**14a**	95
3	**13b**	10	**14b**	95
4	**13c**	10	**14c**	85
5	**13d**	8	**14d**	92
6	**13e**	9	**14e**	92
7	**13f**	12	**14f**	70 (75)[c]
8	**13g**	8	**14g**	45 (80)[c]

[a] Reaction performed on a 20 mmol scale at 25 °C (see experimental section). [b] Isolated yield by flash chromatography. In parenthesis, GC yields. [c] Reaction performed under table 3 conditions.

The starting monomers as well as the corresponding epoxides appear less sensitive to the reaction conditions than the products reported in Table 4. Besides the reaction parameters discussed above it appears that strain of the unsaturation is also an important factor. It is well known that increasing the strain of a double bond increases its nucleophilic reactivity. This property accounts for the excellent selective oxidation yields observed in runs 1 to 6. However, the corresponding epoxides appeared very stable under, for example, acidic conditions. The reasons for such a particular stability are currently unclear.

Conclusion

From this work, it appears that selective epoxidation of unsaturated (meth)acrylic esters may be easily performed by using the Na_2WO_4 - H_2O_2 system under phase transfer catalysis conditions. Rigourous control of the temperature and of the initial pH allows preventing polymerization during these selective epoxidations. Large scale selective epoxidation may be performed under these conditions. It is noteworthy that a very large palet of epoxy (meth)acrylates may be obtained without the tedious purification necessary with classical oxidizing agents. This characteristic, joined to the high chemioselectivity observed, make the above epoxidations very useful.

Experimental Section

GLC analyses were performed by using a Shimadzu GC-8A apparatus, equipped with a Merck D-2500 data processor, with a column of silicone OV-101 (10%) - chromosorb W (3.0 m) (N_2 as carrier gas). ^1H and ^{13}C NMR spectra were measured for deuteriochloroform solutions containing tetramethylsilane (TMS) on a Jeol PMX 60 or Bruker AM 400 spectrometer respectively (J values are given in Hz. Chemical shifts are expressed in ppm (δ)). IR spectra were recorded on a 841 Perkin Elmer spectrophotometer. The HRMS were performed on a Finnigan Mat 95Q at the Centre de Recherche Lorraine from Elf - Atochem (Marienau, France). T.l.c. analyses were performed with hexane - ethyl acetate mixtures (100:0 to 80:20). Products were purified by silica flash chromatography on Kieselgel 60 (230-400 mesh) with petroleum ether - ethyl acetate mixtures as eluent (90:10 to 80:20). All unsaturated (meth)acrylic esters were supplied by ATO (Atochem) and were used as received under air atmosphere after stabilization with hydroquinone monomethyl ether (100 ppm) to avoid polymerization. Their spectroscopic data (IR, ^1H and ^{13}C NMR) were in agreement with the expected formulas and the literature data.

Exploratory experiments.

Epoxidation of 2-methyl-2-propenoic acid, vinylmethyl ester (**5**).

All experiments were performed on a 50 mmoles scale of **5**. Classical procedures refered to in Table 1 were used at an adjusted temperature to avoid polymerization. The reactions were monitored by GC analysis of small aliquots (internal standard was undecan). After completion and classical workup, products were obtained by flash chromatography.

2-methyl-2-propenoic acid, oxiranylmethyl ester (**6**).IR (neat) 2958, 1723, 1639, 1454, 1296, 1171, 942 and 814 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.9 (3H, s, CH_3), 2.4-2.8 (2H, m, CH_2 oxiran), 2.9-3.2 (1H, m, CH oxiran), 3.5-4.55 (2H, m, O-CH_2), 5.5 (1H, s, CH_2 vinyl) and 6.0 ppm (1H, s, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166.35 (CO) 136.1 (MeC=), 126.1 (CH_2=), 65.1 (OCH_2), 49.5

(CH oxiran), 43.8 (CH_2 oxiran) and 17.9 (CH_3). These spectroscopic data were in accordance with those of authentic samples (Elf - Atochem).

Allyl-2-methyl-2,3-oxipropenoic ester (**7**).IR (neat) 2940 (CH), 1740 (CO), 1650 (C=C) and 1300 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.54 (3H, m, CH_3), 2.9 (2H, dd, J = 6 Hz, CH_2 oxiran), 4.6 (2H, d,J = 6 Hz, O-CH_2), 5.05-5.45 (2H, m, CH_2 vinylic) and 5.6-6.2 ppm (1H, m, CH vinylic). These spectroscopic data were in accordance with those of authentic samples (Elf - Atochem).

Epoxidation of 2-methyl-2-propenoic acid, 2-[(octahydro-2, 5-methano-indene oxylethyl ester (**9**).

All experiments were performed on a 20 mmoles scale of **9**. Classical procedures refered to in Table 2 were used at an adjusted temperature allowing to avoid polymerization. The reactions were monitored by GC analysis of small aliquots (internal standard was undecan). After completion and classical workup, products were obtained by flash chromatography.

2-methyl-2-propenoic acid, 2-[(octahydro-2, 5-methano-2H-indeno[1,2-b]oxirenyl)oxylethyl ester (**10**).-IR (neat) 2954 (CH), 1722 (CO), 1639 (C=C), 1297, 1107, 941 and 815 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 0.8-2.5 (13H, m), 2.9-3.7 (5H, m, CH-O), 4.1 (2H, t, O-CH_2, J = 6 Hz), 5.41 (1H, s, CH_2 vinyl) and 5.9 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 167.1 (CO), 136.2 (MeC=), 125.6 (CH_2=), 81.8-77.2 (OCH isomers), 66.0-65.8 (CH_2O isomers), 64.1 (OCH_2), 61.9-59.6 (CH oxiran, isomers), 52.0-39.5 (CH isomers), 39.4-26.0 (CH2 isomers) and 18.3 ppm (CH3); High-resolution MS for $C_{16}H_{22}O_4$ $(M + H)^+$: Calcd m/z: 279.1596; Found : 279.1597.

Epoxidation of various unsaturated (meth)acrylic esters 5, 11a-l and 13f-g.

General procedure.

An aqueous solution prepared from H_2O_2 20% (20 mmol), $Na_2WO_4.2H_2O$ (0.5 mmol) and H_3PO_4 34% (0.85 mmol), at a pH ajusted to 1.9 by a 10% aqueous solution of NaOH, was added at 40°C to a stirred mixture of unsaturated (meth)acrylic esters (10 mmol) and Aliquat 336 (0.2 mmol) in 15 ml of CH_2Cl_2. Disappearance of the substrate was monitored by GC analysis of small aliquots. At the time of complete disappearance of the substrate or no evolution of the reaction, a solution of $FeSO_4$ was added to the reaction mixture, in order to destroy the peroxides. Then the mixture was extracted with CH_2Cl_2 (3 x 50 ml), the combined organic layers were washed with water (2 x 50 ml) and dried over $MgSO_4$. The solvent was removed under vacuum. Epoxy (meth)acrylic esters were isolated by flash chromatography.

2-propenoic acid, oxiranylmethyl ester (**12a**).IR (neat) 3005 (CH), 2953 (CH), 1727 (CO), 1635 (C=C), 1621 (C=C), 1273, 1189, 987 and 854 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 2.4-2.8 (2H, m, CH_2 oxiran), 2.9-3.2 (1H, m, CH oxiran), 3.6-4.5 (2H, m, O-CH_2) and 5.7-6.6 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.1 (CO), 130.8 (CH_2=), 127.3 (CH=), 64.5 (OCH_2), 48.6 (CH oxiran) and 43.8 ppm (CH_2 oxiran); High-resolution MS for $C_6H_8O_3$ $(M + H)^+$: Calcd m/z: 129.0551; Found : 129.0551.

2-methyl-2-propenoic acid, 2-oxiranylethyl ester (**12b**).IR (neat) 2962 (CH), 2939 (CH), 1722 (CO), 1639 (C=C), 1259, 942 and 834 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.5-2.1 (5H, m), 2.2-3.0 (3H, m, CH_2 oxiran, CH oxiran), 4.1 (2H, t, O-CH_2, J = 6 Hz), 5.3 (1H, s, CH_2 vinyl) and 5.9 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166.8 (CO), 136.3 (MeC=), 125.9 (CH_2=), 61.3 (OCH_2), 49.2 (CH oxiran), 46.5 (CH_2 oxiran), 31.6 (-CH_2-) and 17.9 ppm (CH_3); High-resolution MS for $C_8H_{12}O_3$ $(M + H)^+$: Calcd m/z: 157.0864; Found : 157.0869.

2-propenoic acid, 2-oxiranylethyl ester (**12c**).IR (neat) 2927 (CH), 1729 (CO), 1638 (C=C), 1622 (C=C), 1278, 986 and 810 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.6-2.2 (2H, m, -CH_2-), 2.3-3.1 (3H, m, CH_2 oxiran, CH oxiran), 4.2 (2H, t, O-CH_2, J = 6 Hz) and 5.5-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.7 (CO), 130.6 (CH_2=), 128.0 (CH=), 61.1 (OCH_2), 49.1 (CH oxiran), 46.4 (CH_2 oxiran) and 31.5 ppm (-CH_2-); High-resolution MS for $C_7H_{10}O_3$ $(M + H)^+$: Calcd m/z: 143.0708; Found :143.0706.

2-methyl-2-propenoic acid, 4-oxiranylbutyl ester (**12d**).IR (neat) 2930 (CH), 1718 (CO), 1639 (C=C), 1298, 1168, 944 and 810 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.1-2.1 (9H, m), 2.2-3.0 (3H, m, CH_2 oxiran, CH oxiran), 4.0 (2H, t, O-CH_2, J = 6 Hz), 5.4 (1H, s, CH_2 vinyl) and 5.9 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 167.2 (CO), 136.4 (MeC=), 125.2 (CH_2=), 64.6 (OCH_2), 51.9 (CH oxiran), 46.6 (CH_2 oxiran), 32.3, 28.8, 23.0 (-CH_2-) and 18.2 ppm (CH_3); High-resolution MS for $C_{10}H_{16}O_3$ $(M + H)^+$: Calcd m/z: 185.1177; Found : 185.1175.

2-propenoic acid, 4-oxiranylbutyl ester (**12e**).IR (neat) 2943 (CH), 1729 (CO), 1638 (C=C), 1622 (C=C), 1272, 985 and 789 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.1-2.0 (6H, m, -CH_2-), 2.1-2.9 (3H, m, CH_2 oxiran, CH oxiran), 4.0 (2H, t, O-CH_2, J = 6 Hz) and 5.4-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.8 (CO), 130.8 (CH_2=), 128.2 (CH=), 63.9 (OCH_2), 51.6 (CH oxiran), 46.4 (CH_2 oxiran) and 22.9, 28.3, 31.6 ppm (-CH_2-); High-resolution MS for $C_9H_{14}O_3$ $(M + H)^+$: Calcd m/z: 171.1021; Found : 171.1015.

2-methyl-2-propenoic acid, 8-oxiranyloctyl ester (**12f**). IR (neat) 2931 (CH), 1722 (CO), 1640 (C=C), 1260, 939 and 815 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.0-2.0 (17H, m), 2.1-2.9 (3H, m, CH_2 oxiran, CH oxiran), 3.9 (2H, t, O-CH_2, J = 6 Hz), 5.3 (1H, s, CH_2 vinyl) and 5.8 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 167.2 (CO), 136.3 (MeC=), 124.5 (CH_2=), 64.2 (OCH_2), 51.9 (CH oxiran), 46.5 (CH_2 oxiran), 32.5-26.0 (-CH_2-) and 18.1 ppm (CH_3); High-resolution MS for $C_{14}H_{24}O_3$ $(M + H)^+$: Calcd m/z: 241.1803; Found : 241.1802.

2-propenoic acid, 8-oxiranyloctyl ester (**12g**).IR (neat) 2932 (CH), 1727 (CO), 1638 (C=C), 1621 (C=C), 1273, 986 and 833 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) 1.1-1.9 (14H, m, -CH_2-), 2.1-2.9 (3H, m, CH_2 oxiran, CH oxiran), 4.0 (2H, t, O-CH_2, J = 6 Hz) and 5.4-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.8 (CO), 130.0 (CH_2=), 128.3 (CH=), 64.2 (OCH_2), 51.8 (CH oxiran), 46.5 (CH_2 oxiran) and 32.1-25.5 ppm (-CH_2-); High-resolution MS for $C_{13}H_{22}O_3$ $(M + H)^+$: Calcd m/z: 227.1647; Found : 227.1648.

2-methyl-2-propenoic acid, (1-methyloxiranyl)-methyl ester (**12h**).IR (neat) 2972 (CH), 2931 (CH), 1723 (CO), 1639 (C=C), 1295, 942 and 814 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) 1.3 (3H, d, CH_3, J = 5,5 Hz), 1.9 (3H, s, CH_3 vinyl), 2.6-3.3 (2H, m, CH oxiran), 3.7-4.6 (2H, m, O-CH_2), 5.5 (1H, s, CH_2 vinyl) and 6.0 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166.3 (CO), 135.6 (MeC=), 125.4 (CH_2=), 64.4 (OCH_2), 55.7 (CH oxiran), 51.7 (CH oxiran), 17.7 (CH_3 vinyl) and 16.7 ppm (CH_3); High-resolution MS for $C_8H_{12}O_3$ $(M + H)^+$: Calcd m/z:157.0864; Found : 157.1865.

2-propenoic acid, (1-methyloxiranyl)-methyl ester (**12i**).IR (neat) 2932 (CH), 1732 (CO), 1635 (C=C), 1621 , 1274, 984 and 809 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) 1.3 (3H, d, CH_3, J = 5,5 Hz), 2.6-3.1 (2H, m, CH oxiran), 3.6-4.5 (2H, m, O-CH_2) and 5.5-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.4 (CO), 131,0 (CH_2=), 127.6 (CH=), 64.4 (OCH_2), 55.8 (CH oxiran), 52.1 (CH oxiran) and 16.8 ppm (CH_3); High-resolution MS for $C_7H_{10}O_3$ $(M + H)^+$: Calcd m/z: 143.0708; Found : 143.0710.

2-methyl-2-propenoic acid, (1,1'-methyloxiranyl)-methyl ester (**12j**).IR (neat) 2929 (CH), 1724 (CO), 1639 (C=C), 1294, 940 and 814 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) 1.3 (6H, m, CH_3), 1.9 (3H, s, CH_3 vinyl), 2.8 (1H, t, CH oxiran, J = 6 Hz), 3.7-4.4 (2H, m, O-CH_2), 5.4 (1H, s, CH_2 vinyl) and 5.9 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166.9 (CO), 135.7 (MeC=), 125.2 (CH_2=), 63.7 (OCH_2), 60.5 (CH oxiran), 57.9 (-C- oxiran), 24.3, 18.7 (CH_3) and 18.0 ppm (CH_3 vinyl); High-resolution MS for $C_9H_{14}O_3$ $(M + H)^+$: Calcd m/z: 171.1021; Found : 171.1025.

2-propenoic acid, (1,1'-methyloxiranyl)-methyl ester (**12k**).IR (neat) 2968 (CH), 2932 (CH), 1729 (CO), 1636 (C=C), 1621 (C=C), 1264, 987 and 809 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) 1.2 (6H, m, CH_3), 2.8 (1H, t, CH oxiran, J = 6 Hz), 3.7-4.4 (2H, m, O-CH_2) and 5.5-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl);; ^{13}C NMR ($CDCl_3$,75 MHz) 165.7 (CO), 131.6 (CH_2=), 127.9 (CH=), 63.0 (OCH_2), 60.4 (CH oxiran), 58.1 (-C- oxiran) and 24.4, 18.7 ppm (CH_3); High-resolution MS for $C_8H_{12}O_3$ $(M + H)^+$: Calcd m/z: 157.0864; Found : 157.0864.

2-methyl-2-propenoic acid, (1-phenyloxiranyl)-methyl ester (**12l**).IR (neat) 2987 (CH), 2958 (CH), 1714 (CO), 1639 (C=C), 1608, 1579, 1498 (C=C, aromatic), 1295, 945 and 814 cm^{-1}. ^1H NMR (CCl_4, 60 MHz) 1.9 (3H, s, CH_3 vinyl), 2.9-3.2 (1H, m, CH oxiran), 3.6 (1H, d, CH oxiran, J = 2 Hz), 3.8-4.6 (2H, m, O-CH_2), 5.4 (1H, s, CH_2 vinyl), 6.0 (1H, s, CH_2 vinyl) and 7.0 ppm (5H, m, aromatic); ^{13}C NMR ($CDCl_3$,75 MHz) 166.5 (CO), 136.0 (-C- aromatic), 135.5 (MeC=), 128.5, 128.2

(CH= aromatic), 125.9 (CH_2=), 125.4 (CH= aromatic), 64.1 (OCH_2), 58.9 (CH oxiran), 55.9 (Ph-CH oxiran) and 17.9 (CH_3); High-resolution MS for $C_{13}H_{14}O_3$ $(M + H)^+$: Calcd m/z: 219.1021; Found : 219.1022.

2-propenoic acid, (1-phenyloxiranyl)-methyl ester (**12m**).IR (neat) 2994 (CH), 2952 (CH), 1731 (CO), 1635 (C=C), 1620 (C=C), 1601, 1579, 1498 (C=C, aromatic),1295, 984 and 809 cm^{-1}. ^1H NMR (CCl_4,60 MHz)2.9-3.2 (1H, m, CH oxiran), 3.6 (1H, d, CH oxiran, J = 2 Hz), 3.8-4.5 (2H, m, O-CH_2), 5.5-6.5 (3H, m, CH_2 vinyl, CH vinyl) and 7.0 ppm (5H, m, aromatic); ^{13}C NMR ($CDCl_3$,75 MHz) 165.4 (CO), 136.0 (-C- aromatic), 131.3 (CH_2=), 128.2 (CH= vinyl), 128.1 , 127.5, 125.4 (CH= aromatic), 64.0 (OCH_2), 58.9 (CH oxiran) and 56.0 ppm (Ph-CH oxiran); High-resolution MS for $C_{12}H_{12}O_3$ $(M + H)^+$: Calcd m/z: 205.0864; Found : 205.0871.

2-methyl-2-propenoic acid, 5(or 6)-oxiranylbicyclo[2.2.1]hept-2-yl ester (**14f**).IR (neat) 2966 (CH), 1724 (CO), 1638 (C=C), 1263, 988 and 814 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 0.8-3.6 (15H, m), 4.4-4.8 (1H, m, CO-OCH), 5.4 (1H, s, CH_2 vinyl) and 5.9 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166.6 (CO), 136.3 (MeC=), 124.9 (CH_2=), 77.5 (O-CH_2 oxiran), 76.9-76.5 (OCH isomers), 56.5-34.8 (CH isomers), 40.1-20.0 (CH_2 isomers) and 17.9 ppm (CH_3).; High-resolution MS for $C_{13}H_{19}O_3$ $(M + H)^+$: Calcd m/z: 223.1334; Found : 223.1326.

2-propenoic acid, 5(or 6)-oxiranylbicyclo[2.2.1]hept-2-yl ester (**14g**).IR (neat) 2967 (CH), 1723 (CO), 1635 (C=C), 1619 (C=C), 1272, 987 and 811 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.0-3.2 (12H, m), 4.3-4.8 (1H, m, CO-OCH), 5.4-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.1 (CO), 129.9 (CH_2=), 128.5 (CH=), 77.2 (O-CH_2 oxiran), 76.9-76.4 (OCH isomers), 54.3-37.9 (CH isomers) and 40.9-22.0 ppm (CH_2 isomers); High-resolution MS for $C_{12}H_{17}O_3$ $(M + H)^+$: Calcd m/z: 209.1177; Found : 209.1177.

Epoxidation of various unsaturated (meth)acrylic esters 9, 13a-g.

General procedure.

An aqueous solution prepared from H_2O_2 20% (20 mmol), $Na_2WO_4.2H_2O$ (0.25 mmol) and H_3PO_4 34% (0.425 mmol), at a pH ajusted to 1.7 by a 10% aqueous solution of NaOH, was added at room temperature to a stirred mixture of unsaturated (meth)acrylic esters (10 mmol) and Aliquat 336 (0.1 mmol) in 15 ml of CH_2Cl_2. Disappearance of the substrate was monitored by GC analysis of small aliquots. At the time of complete disappearance of the substrate or no evolution of the reaction, a solution of $FeSO_4$ was added to the reaction mixture, in order to destroy the peroxides. Then the mixture was extracted with CH_2Cl_2 (3 x 50 ml), the combined organic layers were washed with water (2 x 50 ml) and dried over $MgSO_4$. The solvent was removed under vacuum. Epoxy (meth)acrylic esters were isolated by flash chromatography.

2-propenoic acid, 2-[(octahydro-2, 5-methano-2H-indeno[1,2-b]oxirenyl)oxy]ethyl ester (**14a**). IR (neat) 2953 (CH), 1725 (CO), 1636 (C=C), 1620 (C=C), 1270, 1112, 926 and 836 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 0.8-2.6 (10H, m), 3.0-3.7 (5H, m, CH-O), 4.1 (2H, t, O-CH_2, J = 6 Hz) and 5.5-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.7 (CO), 130.5 (CH_2=), 128.0 (CH=), 81.6-76.9 (OCH isomers), 66.0-65.6 (CH_2O isomers), 63.5 (OCH_2), 61.5-59.1 (CH oxiran, isomers), 51.4-39.6 (CH isomers), 39.2-25.7 ppm (CH2 isomers); High-resolution MS for $C_{15}H_{20}O_4$ $(M + H)^+$: Calcd m/z: 265.1439; Found : 265.1440.

2-methyl-2-propenoic acid, [(octahydro-2, 5-methano-2H-indeno[1,2-b]oxirenyl)]ester (**14b**). IR (neat) 2962 (CH), 1717 (CO), 1638 (C=C), 1264, 989 and 815 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1.0-2.6 (13H, m), 2.9-3.4 (2H, m, CH oxiran), 4.3-4.8 (1H, m, OCH), 5.3 (1H, s, CH_2 vinyl) and 5.8 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166.6 (CO), 136.3 (MeC=), 124.8 (CH_2=), 76.4 (OCH isomers), 61.0-60.5 (CH oxiran, isomers), 49.7-40.0 (CH isomers), 39.0-28.0 (CH2 isomers) and 17.9 ppm (CH3); High-resolution MS for $C_{14}H_{18}O_3$ $(M + H)^+$: Calcd m/z: 235.1334; Found : 235.1334.

2-propenoic acid, [(octahydro-2, 5-methano-2H-indeno[1,2-b]oxirenyl)]ester (**14c**): IR (neat) 2962 (CH), 1729 (CO), 1636 (C=C), 1619 (C=C), 1240, 986 and 810 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 0.8-

2.6 (10H, m), 3.0-3.5 (2H, m, CH oxiran), 4.3-4.7 (1H, m, OCH) and 5.4-6.4 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 165.4 (CO), 130.1 (CH_2=), 128.5 (CH=), 76.4 (OCH), 61.1-60.6 (CH oxiran, isomers), 49.7-40.7 (CH isomers) and 39.0-29.7 ppm (CH_2 isomers); High-resolution MS for $C_{13}H_{16}O_3$ $(M+H)^+$: Calcd m/z: 221.1177; Found : 221.1175.

2-methyl-2-propenoic acid, 5(or 6)-(methyl-spiro oxiranyl)bicyclo[2.2.1]hept-2-yl-ester (**14d**): IR (neat) 2964 (CH), 1718 (CO), 1638 (C=C), 1301, 942 and 814 cm^{-1}. ^1H NMR (CCl_4,60 MHz) 1,2 (3H, d, CH_3, J = 5 Hz), 0,7-2,6 (11H, m), 2,6-3,1 (1H, m, CH oxiran), 4,5-4,8 (1H, m, OCH), 5,3 (1H, s, CH_2 vinyl) and 5,8 ppm (1H, s, CH_2 vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 166,1 (CO), 135,9 (MeC=), 124,7 (CH_2=), 73,6-72,9 (OCH isomers), 66,8 (C-O), 58,7-34,6 (CH isomers), 38,5-33,2 (CH_2 isomers), 17,6 (CH_3 vinyl) and 15,4-14,7 ppm (CH_3 isomers); High-resolution MS for $C_{13}H_{18}O_3$ $(M+H)^+$: Calcd m/z: 223.1334; Found : 223.1332.

2-propenoic acid, 5(or 6)-(methyl-spiro oxiranyl)bicyclo[2.2.1]hept-2-yl-ester (**14e**): IR (neat) 2970 (CH), 1723 (CO), 1635 (C=C), 1619 (C=C), 1273, 984 and 810 cm^{-1}. ^1H NMR (CCl_4,60 MHz)1.2 (3H, d, CH_3, J = 5 Hz), 0.7-2.6 (8H, m), 2.6-3.2 (1H, m, CH oxiran), 4.5-4.8 (1H, m, OCH) and 5.5-6.5 ppm (3H, m, CH_2 vinyl, CH vinyl); ^{13}C NMR ($CDCl_3$,75 MHz) 164.9 (CO), 129.9 (CH_2=), 128.1 (CH=), 73.6-73.1 (OCH isomers), 66.7 (C-O), 56.5-35.1 (CH isomers), 38.5-33.8 (CH_2 isomers) and 15.4-14.6 ppm (CH_3 isomers); High-resolution MS for $C_{12}H_{16}O_3$ $(M+H)^+$: Calcd m/z: 209.1177; Found : 209.1182.

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