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Synthesis of Methacrylic-type Peroxidic Compounds and Study of Their Homolytic Induced Decomposition in Solution

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Abstract: Various unsaturated peroxidic compounds have been prepared, characterized and inductively decomposed in various solvents to afford the corresponding oxiranes. The reaction proceeded by a radical chain mechanism and was initiated either by thermolysis of added *t*-butyl peracetate at 110°C or AIBN at 80°C, or by autoxidation of BEt_3 at 20°C. The studied peroxyderivatives were designed to generate oxyl radicals reacting either by isomerization (*e.g.* intramolecular 1,5-hydrogen atom transfer, cyclization or β-scission of a cyclic structure), fragmentation or hydrogen atom transfer to solvents to yield functional alkyl radicals.

INTRODUCTION

Over the past five years, several works have shown the synthetic potential of the induced decomposition of peroxidic compounds bearing an activated unsaturation. Numerous glycidic esters were prepared by the use of methacrylic-type peroxidic compounds as reagents (not as initiators) in radical reactions[1,2,3,4]. These unsaturated peroxyderivatives have also been employed in radical polymerization as efficient, functionalized regulators[5,6,7]. Their applications in stereoselective reactions[8] were reported recently as well. As shown in Fig. 1, a new function is created in the intramolecular homolytic substitution (S_Hi) reaction on the O-O bond, a second one being produced by evolution of the eliminated oxy radical ZO•. The Fig. 1 summarizes the peroxyderivatives prepared to fill such conditions and the oxiranes obtained in this work. In the present article, carbon-centered radicals R• are generated from oxyl radicals ZO• in three ways: (1) hydrogen abstraction from a solvent RH[1,2] or (2) isomerization [via β-scission of a cyclic radical, cyclisation or 1,5-H translocation of oxyl radicals to alkyl ones][3] and (3) fragmentation [*e.g.* β-scission of adjacent C-C bond][4]. The following results complete the preliminary studies realized according to these three strategies of generation of alkyl radicals. Advantages and drawbacks of each method are discussed.

RESULTS AND DISCUSSION

Preparation of peroxydic compounds.

Peroxides **2-9** were easily synthesized according to Navarro *et al.*[9] by condensation of the corresponding alkyl hydroperoxides in basic medium with *(E)*-ethyl 2-bromomethylbutanoate[10] (Fig. 2). The fair yields obtained for the synthesis of these peroxides seems to be due essentially to difficulties in their purification and production of some side-products[9].

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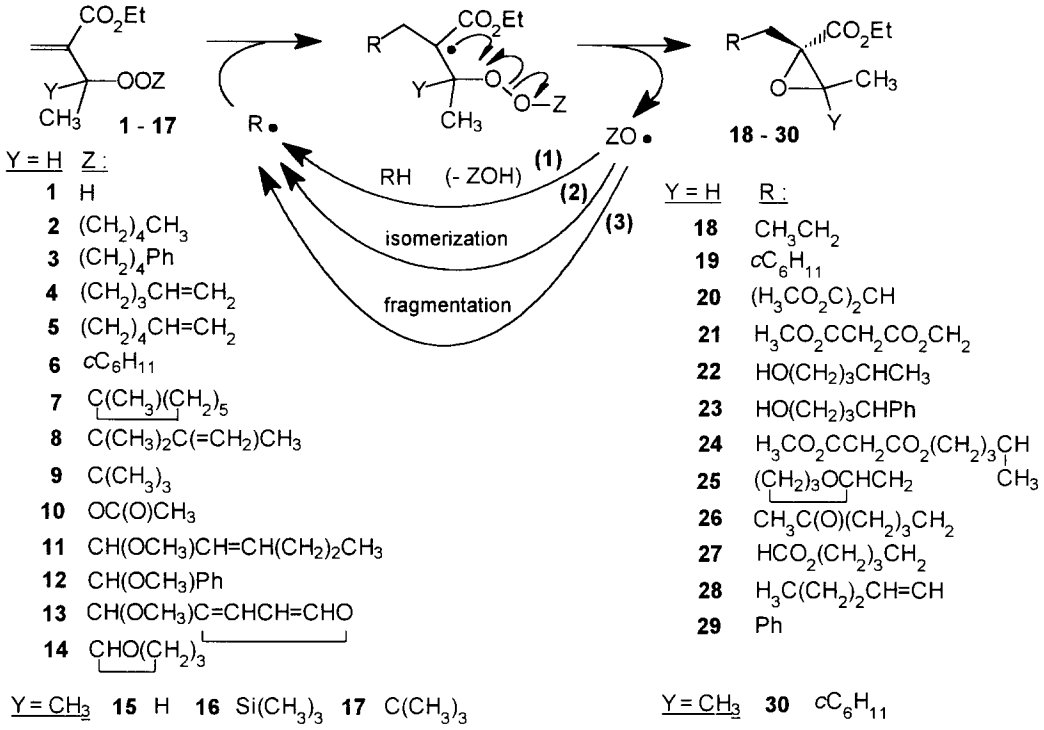


Fig. 1. General mechanism for the radical induced decompositions of peroxyderivatives 1-17.

The synthesis of the secondary peroxide **6** by reaction of the cyclohexyl hydroperoxide with *(E)*-ethyl 2-bromomethylbutanoate was unsuccessfull, because of the basicity of the medium which involves degradation of secondary peroxyderivatives[11]. The same failure was observed for the reaction of the former bromide or 4-pentenyl bromide with the hydroperoxide **1**. Peroxides **7** and **8** were obtained from the corresponding tertiary hydroperoxides under basic conditions. Condensation of **1** with the trichloroacetimidates of 1-methylcyclohexanol and *t*-butanol, in the presence of catalytic amount of trifluoroboran etherate, appeared to be a more efficient route to afford tertiary peroxides **7** and **9** respectively, in good yields (Fig. 2). This useful method was adapted by Maillard *et al.*[12] from a preparation of tertiary ethers and has the advantage that secondary hydroperoxide **1** can be used as reagent under non-basic conditions. Hydroperoxide **15** was obtained easily by quantitative photooxygenation[13] of ethyl 2,3-dimethylbut-2-enoate, the latter being prepared by dialkylcuprate coupling to the enol phosphate of a β-ketoester[14] in good yield (Fig. 3). In this procedure, most of the product was often lost during synthesis and purification. The purity of **15** was confirmed by an active oxygen titration[15].

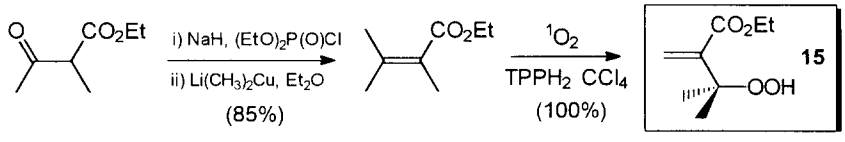
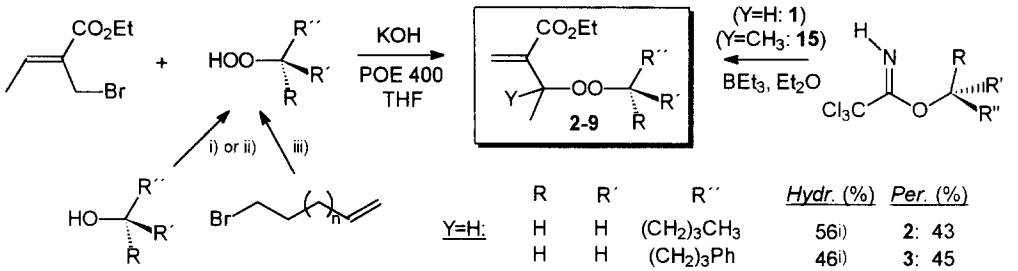


Fig. 3. Synthesis of **15** by photooxygenation of ethyl 2,3-dimethylbut-2-enoate.

Peroxysilane **16** was quantitatively prepared by condensation of **15** on trimethylsilyl chloride, in basic medium (pyridine), according to the general experimental procedure described by Buncel *et al.*[16] and adapted by Colombani *et al.*[2]. Peroxide **17** was not available by the general reaction of *t*-butyl hydroperoxide with ethyl

2-bromomethyl-3-methylbutanoate, due to steric hindrance which disfavoured the SN_2' process. It was however obtained in good yield by reaction of **15** with *t*-butyl trichloroacetimidate (Fig. 2).



	R	R'	R''	Hydr. (%)	Per. (%)
Y=H:	H	H	$(CH_2)_3CH_3$	56i)	**2**: 43
	H	H	$(CH_2)_3Ph$	46i)	**3**: 45
	H	H	$(CH_2)_2CH{=}CH_2$	35iii)	**4**: 47
	H	H	$(CH_2)_3CH{=}CH_2$	40iii)	**5**: 45
	$(CH_2)_5$		H	15i)	**6**: /
	$(CH_2)_5$		CH_3	28ii)	**7**: 26, 35v)
	CH_3	CH_3	$C(=CH_2)CH_3$	85iv)	**8**: 30
	CH_3	CH_3	CH_3		**9**: 78v)
Y=CH_3:	CH_3	CH_3	CH_3		**17**: 47v)

i) CH_3SO_2Cl, pyridine, 2 h, 0°C; H_2O_2 (36% aq.), KOH, MeOH/H_2O, 12 h, 0-20°C.
ii) H_2O_2 (36% aq.), H_2SO_4 (69% aq.), 24 h, 0°C. iii) H_2O_2 (36% aq.), KOH, MeOH/H_2O, 12 h, 0-20°C.
iv) $(H_3C)_2C{=}C(CH_3)_2$, $^1O_2$, sens., CCl_4, hν, 1 h, -15°C. v) from *t*-butyl acetimidates

Fig. 2. Synthesis of peroxides **2-8** from the corresponding hydroperoxides or *tert*-alkyl acetimidates.

Various methods were investigated to prepare the perester **10** in good yield (Fig. 4). The Harmon method[17], based on the condensation of **1** with a diketene under acidic conditions, caused a vigorous decomposition of the reaction mixture whereas reaction of **1** with *N,N*-dicyclohexylcarbodiimide[18] or *N,N'*-carbonyldiimidazole (Imi)[19], in the presence of acetic acid failed. In the latter case, formation of epoxide **31** by Michael addition of imidazole on the double bond bearing an electron-withdrawing group was observed. Such behaviour has already been noted in the synthesis of *t*-butyl peracrylate from acrylic acid and *N,N'*-carbonyldiimidazole[20]. It is the procedure of Milas *et al.*[21] which permit to access to perester **10** in relatively fair yield, due to the instability of secondary hydroperoxides in basic medium[11].

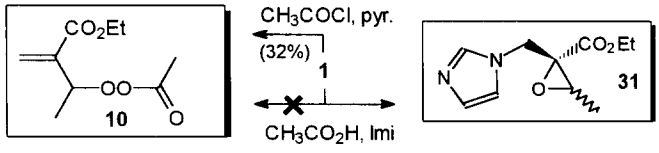


Fig. 4. Synthesis of ethyl 3-acetyldioxy-2-methylenebutanoate **10** and achievement of ethyl 2,3-epoxy-2-(1-imidazolylmethyl)butanoate **31** as side-product.

The addition of **1** on 3-trimethylsilyl-2-oxa-1-butene in the presence of a catalytic amount of *p*-toluenesulphonic acid (APTS) does not give the expected peroxyketal **32** but afford fair yields of the alcohol **34** and its methyl acetate **35** (Fig. 5). A spontaneous isomerization of **32**, yielding the 2-ethoxycarbonyl-1-methyl-2-propenyl methyl trimethylsilyl orthoacetate **33**, which was subsequently hydrolyzed, could explain the formation of the obtained compounds. Indeed, tertiary alkyl peroxides are also known to undergo acid-catalysed oxygen-oxygen heterolysis by a nucleophilic 1,2-rearrangement[22]. In these rearrangements, the bond-

fission and bond-formation processes are all synchronous[23]. The hydrolysis of **33** could also lead to the formation of low boiling « alcohols » (MeOH, Me_3SiOH) and trimethylsilyl acetate or methyl acetate.

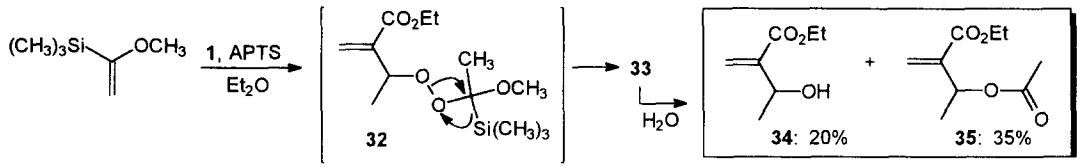
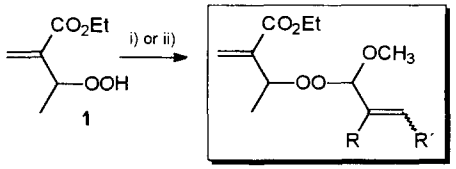


Fig. 5. Isomerization of peroxyketal **32**, under acidic conditions.

The synthesis of peroxyketal **11** (78% yield) was performed by reaction of **1** on the corresponding dimethylketal with elimination of the produced methanol under reduced pressure[24]. As well, peroxyketals **12** and **13** were easily obtained in a one pot synthesis in 73 and 60% yields (Fig. 6) from benzaldehyde and furfuraldehyde respectively, according to a procedure previously described[4].



	R	R'		
11[i)]	$(CH_2)_2CH_3$	H	(78%)	i) $(H_3CO)_2CH\text{-}CH{=}CH(CH_2)_2CH_3$, APTS, in vacuo, 1 h, 20°C.
12[ii)]	CH=CH-CH=CH		(73%)	
13[ii)]	CH=CHO		(60%)	ii) R'CH=C(R)CHO, $HC(OCH_3)_3$, APTS, 2 h, 20°C.

Fig. 6. Preparation of peroxyketals **11-13**.

Induced decomposition of peroxydic compounds.

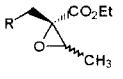
The induced decomposition of peroxides **2-4** and 7 and peroxyketals **11-14**, with *t*-butyl peracetate **36** as initiator, have been investigated in benzene. Preliminary results of a part of this work have already been briefly reported[3], without any details on their synthesis, characterization, and reactivity. In the present paper, the various induced reactions, involved in the homolysis of compounds **2** and **14**, have also been investigated in detail through the thermolysis of *t*-butyl peracetate **36** in solutions in solvents bearing homolytically transferable hydrogens (cyclohexane and dimethyl malonate). The two main radical routes for the disappearance of the mentioned peroxyderivatives have been investigated through the chemical analysis of the reaction products. They can be decomposed either by an intramolecular homolytic substitution (S_Hi) of the adduct radical on the O-O bond, following an addition step on the activated unsaturation or by a β-scission of the radical formed consecutively to the transfer of an allylic or an acetalic hydrogen on the peroxyderivative. In each case, oxyl radicals produced in these two processes were shown to react either by an isomerization reaction, or a fragmentation (leading to a carbon-centered radical and a carbonyl derivative, *e.g.* an ester), or a hydrogen abstraction from the solvent to generate alkyl radicals.

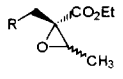
Isomerization of oxyl radicals in various solvents. The alkoxyl radicals studied above were designed to react by diverse types of isomerization reaction, leading to carbon-centered radicals: an intramolecular 1,5-hydrogen transfer, a β-scission of a cyclic fragment or a cyclization, which is the reverse reaction of the former.

Isomerization by 1,5-hydrogen transfer: The homolytic induced decomposition of peroxides **2** and **3** leads to the formation of *n*-pentyloxyl and 4-phenylpentyloxyl radicals, respectively. These radicals evolve through a 1,5-intramolecular hydrogen transfer reaction to generate the corresponding 4-hydroxy-(1-methyl or 1-phenyl)butyl radicals, which can add respectively to **2** or to **3** to afford epoxides **22** and **23** in good and fair yields. In the case of substituted carbon-centered radicals, and particularly those bearing a stabilizing group like an aromatic fragment, dimerization reaction was shown to be a non-negligible pathway[25]. Such a phenomenon has been particularly observed for the induced decomposition of **3** in benzene, decreasing the yield of the epoxide **23**. Only 40% of isolated compounds (46% by GC analysis) were obtained. In order to investigate the

efficiency of the intramolecular reaction in the presence of solvents bearing homolytically transferable hydrogens, the evolution of *n*-pentyloxyl radicals, yielded by the induced decomposition of **2**, have been studied in cyclohexane, dimethyl malonate, and benzene. The results are compiled in the Table 1.

Tables 1 and 2. Yields of isolated epoxides and undistilled high-boiling products produced in the induced decomposition of **2** (left) and **14** (right) in cyclohexane, dimethyl malonate and benzene, at 110°C[a][b].

2	cC_6H_{12}	$CH_2(CO_2Me)_2$	PhH
22	(52) 48	(2)	(82) 80
24	/	(75) 70[c]	/
	**19**: (38) 36	**20**: (9) **21**: (< 1)	/
pentanol	(36)	(2)[d]	(10)
allylic H transfer[e]	10	14[f]	18

14	cC_6H_{12}	$CH_2(CO_2Me)_2$	PhH
27	(88) 75	(60) 58	(86) 71
HCO_2n-Bu	(6)	(5)	(8)
	**19**: (8) 7	**20**: (9) 5[c]	/
HO-THP[d]	(1)	/	(2)
other H transfers[e]	9	33[f]	14

[a] molar ratio solvent / **2** / **36** = 20 / 1 / 0.1. [b] between parentheses, GC yields based on **2**. [c] compound **24** was prepared by quantitative transesterification of 1.0 g of the alcohol-epoxide **22** in dimethyl malonate at 110°C during 12 hours, with a molar ratio epoxide / solvent = 1 / 20. [d] as methyl pentyl malonate, formed as **24** by total transesterification of pentanol in dimethyl malonate under the same conditions. [e] estimation of allylic attack, calculated from GC data as: 100% - (% **22**) - (% **20-21**). [f] traces of bis(dimethyl malonyl)[26] were also detected.

[a] molar ratio solvent / **14** / **36** = 20 / 1 / 0.1. [b] between parentheses, GC yields relative to **14**. [c] as a mixture of the corresponding two isomers **20** (major) and **21** (traces). [d] THP-OH: 2-hydroxytetrahydropyrane. [e] estimation of allylic and/or ketalic attack, calculated from GC data as: 100% - (% **27**) - (% **20-21**). [f] considering that the occurence of allylic hydrogen transfer is maximum in benzene, the present result may include also high-boiling products of transesterification.

n-Pentyloxyl radicals can compete either for 1,5-H transfer or intermolecular hydrogen abstraction from the molecule itself (*e.g.* in allylic position) or from the solvent, respectively. As shown in previous papers[2], the efficiency of the intramolecular hydrogen abstraction by the oxyl radicals, compared to the hydrogen abstraction from the solvents or from the peroxide itself, can be estimated from the relative proportion of **22** compared to the amount of the adducts of the solvents (*e.g.* epoxides **19** or **20-21**), the latter being also correlated to the amount of pentanol. In all cases, the major product of the induced decomposition of peroxide **2** is epoxide **22**, and this result is maximized when the solvent is benzene. Oxiranes **19** or **20-21**, formed by addition of radicals transfered from the solvent to **2**, were also obtained as minor products, regardless of the solvent used. A possible consumption of the alcohol-type molecules formed in situ by transesterification reaction[27] has also to be taken into account in dimethyl malonate to explain accurately the evolution of *n*-pentyloxyl radicals. The efficiency of the transesterification reaction depends also on the nature of the alcohol involved. A test reaction has shown that the heating of a 0.05 M solution of pentanol in dimethyl malonate at 110°C during 12 hours afforded total transesterification whereas reaction of *t*-butanol led only to 62% of *t*-butyl methyl malonate and an equivalent amount of methanol, 38% of *t*-butanol being recovered unchanged.

Hydrogen atom transfer from cyclohexane was recently reported to be easier than from dimethyl malonate, in the case of a series of alkoxyl radicals[2]. According to this result, the efficiency of the intramolecular hydrogen abstraction appears to be better from dimethyl malonate than from cyclohexane and the formation of **22** is higher in the former solvent. The presence of the two epoxides **20** and **21**, produced by hydrogen transfer on dimethyl malonate, was checked by GC analysis. However, only the oxirane **20**, produced by addition of $(H_3CO_2C)_2CH\bullet$, was observed in non-negligible yield. The very low amount of **21** (< 1%), which would be formed by addition of $H_3CO_2C\text{-}CH_2\text{-}CO_2CH_2\bullet$ to peroxide **2**, indicates a regiospecific nucleophilic attack of the

secondary 5-hydroxypent-2-yl radicals on the methylene fragment (presence of hydrogens on an electron-deficient site) of dimethyl malonate, agreeing with a similar regioselectivity observed in the case of methyl radicals under similar conditions[2]. Traces of **21** could result only from H abstraction from the methyl fragments of the diester either by electrophilic pentyloxyl radicals generated in the S_Hi reaction (*ca.* 2% of methyl pentyl malonate, *i.e.* pentanol equivalent, detected) or by *t*-butoxyl radicals formed in the homolysis of **36**.

The induced decomposition of **5** in benzene at 110°C yielded by distillation *ca.* 25% of a mixture, relative to the starting material. The low yield observed could be attributed to two main causes: induced decomposition of the peroxyderivatives by allylic hydrogen abstraction (presence of several kinds of allylic hydrogens) and/or dimerization of the allylic radicals 6-hydroxyhex-2-enyl **37** and 1-ethenyl-4-hydroxybutyl **38**, formed through the 1,5-hydrogen atom transfer of hex-5-enyloxyl radicals. This latter process is generally known to be more efficient than the addition to the unsaturation of the peroxide. Allyl radicals are known to produce coupling products as it was the case for 2-cyclohexenyl radicals in the induced decomposition of ethyl 2-*t*-butylmethylpropenoate in cyclohexene[1]. ^{13}C NMR analysis of the mixture seemed to indicate a large proportion of product bearing fragments in good agreement with **37** but the presence of ethylenic carbons of a terminal double bond revealed also a small number of compounds from reaction of **38**. The presence of this compound was supported by ^1H NMR chemical shifts of fragment $H_2C{=}CH$ (4.8-4.6 ppm, low intensity) and from ^{13}C NMR chemical shifts of sp^2 carbons (*ca.* 115 and 140 ppm). The analysis of this mixture has not been investigated further but the multiple evolutions of hex-5-enyloxyl radicals have already been reported by Surzur *et al.*[28].

Isomerization by β-scission: The major products formed in the induced decomposition of **14** in cyclohexane, dimethyl malonate, and benzene were distilled and identified. Yields of isolated compounds appear in Table 2 with the corresponding GC measurements. The 2-tetrahydropyranyloxyl radicals evolve nearly exclusively by quantitative fragmentation of the adjacent C-C bond (314 $kJ.mol^{-1}$, calculated by the method of Jørgensen *et al.*[29]) rather than β-scission of the C-O bond (335 $kJ.mol^{-1}$)[29]. A comparison of the data obtained in the present work with those previously reported in the case of the generation of $CH_3\bullet$ from the reaction of ethyl 1-methoxy-1-methylethyldioxy-2-methylenebutanoate[2] under the same conditions indicates that the addition of primary alkyl radicals $OHC\text{-}O\text{-}(CH_2)_3\text{-}CH_2\bullet$ is more favoured than hydrogen abstraction from the solvents, in each case. This is in good agreement with a slower hydrogen abstraction from cyclohexane by primary radicals than by methyl ones, and a faster addition of primary alkyl radicals than methyl ones to electron-deficient double bonds.

The formation of epoxide **27** as the major product of the induced decomposition of **14** (whatever the solvent) indicates that 4-formyloxybutyl radicals preferably add to the unsaturation of **14** rather than decaying by way of hydrogen abstraction from solvent (in the case of cyclohexane and dimethyl malonate). This behaviour is quite similar to that observed for the 4-hydroxy-1-methylbutyl radicals. The intramolecular evolution of 2-tetrahydropyranyloxy radicals (*e.g.* β-scission of the C-C bond) is also fast enough to compete with the hydrogen abstraction from the solvent. The presence of 2-hydroxytetrahydropyrane, which would be formed by hydrogen transfer from tetrahydropyranyl radicals, was only detected in a very small amount (*ca.* 1-2%) in each of these solvents. Such a result indicates that hydrogen transfer to the solvent is mostly due to 4-formyloxybutyl radicals, which was confirmed by the GC analysis of butyl formate (Table 2).

In the case of the induced decomposition of **14** in dimethyl malonate, both a high yield of epoxide **27** and a large amount of residue seemed to indicate the presence in the residue of "malonate moieties", which could correspond to the presence of transesterification product of the ester-oxirane **27**. If one considers that allylic hydrogen transfer is maximum in benzene (no possibility of other hydrogen transfer), an estimation of the proportion of **27** consumed by transesterification can be calculated from the difference between the amount of residue in dimethyl malonate and benzene: 33 - 14 = 19%. Thus, the estimated amount of **27**: 60 + 19 = 79%, is close to the proportion of **27** obtained in the other solvents (Table 2).

A 6-membered, concerted dihydrogen elimination was also recently reported in the thermal decomposition of secondary methacrylic-type peroxyketals[4] to explain in part the presence of high-boiling products beside the expected epoxides. This reaction occurred with formation of methyl alkanoate and ethyl 2-methylene-3-oxobutanoate, which homopolymerized to yield oligomers. The formation of H_2, if it occurred under these conditions, is anyway limited to a low extent, considering the high yields of the epoxides obtained (Table 2). The cyclic structure of the peroxide **14** could disfavour the required cyclic-type conformation for H_2 elimination, increasing the activation energy of the reaction.

A study of the influence of the temperature on the induced decomposition of **14** was attempted at 80°C, using AIBN as the initiator, to try to decrease drastically the effect of temperature-dependent reactions. There was a significant effect of the relative molar ratio benzene / **14** / AIBN, at 80°C on the induced decomposition of peroxyketal **14**. With a molar ratio solvent / **14** / AIBN = 20 / 1 / 0.1, epoxide **27** was obtained in 91% yield whereas in the case of a molar ratio 1 / 1 / 0.1, only 55% yield was detected, with non-negligible amount of remaining peroxyketal **14**. Such a phenomenon could be one of the consequences of side-reactions of allylic and/or ketalic hydrogen abstraction, which produce stabilized radicals and inhibit the radical chain reaction.

The reactivity of the 1-methylcyclohexyloxyl radicals, generated by induced decomposition of peroxide **7**, was also investigated in benzene. The formation of 1-methylcyclohexanol, which could be provided by allylic hydrogen abstraction from **7**, has not been detected. 1-Methylcyclohexyloxyl radicals evolved quickly by selective β-scission of a C-C bond of the cycle (314 $kJ.mol^{-1}$) to afford the isomeric 6-oxoheptyl radicals. The elimination of a methyl radical with formation of cyclohexanone, requiring the fragmentation of a C-C bond of higher energy (*ca.* 326 $kJ.mol^{-1}$), was not observed. This functional radical can add to the unsaturation of **7** to afford the ketone-epoxide **26**, which was isolated in 60% yield. This result is of the same order of magnitude as the yield of the ester-epoxide **27** (71% in isolated compound), obtained from the reaction of **14** under the same conditions in benzene.

Isomerization by cyclization: The pent-4-enyloxyl radicals, liberated in the induced decomposition of **4**, can evolve either by intermolecular hydrogen transfer or cyclization[30]. In benzene, the heterocyclic 5-membered rings are easily formed by an irreversible and strictly selective[31] cyclization of the oxygen-centered radicals. In comparison to its carbon counterparts, oxygen radicals show enhanced reactivity and high cyclization rates ($k_c \sim 10^8$ s^{-1}). However, the possibilities of competitive allylic hydrogen abstraction have to be taken into account to explain the fair yield of the THF-epoxide **25** (*ca.* 53% in isolated compound).

Fragmentation by β-scission of oxyl radicals. The induced decomposition of **11** at 110°C during 12 hours in benzene afforded the epoxide **28** in 20% yield of the isolated compound, with a large amount of undistilled high-boiling products but no remaining peroxide. Taking into account that the radical ketalic hydrogen transfer and the non-radical dihydrogen elimination[32] mentioned in the induced decomposition of **14** are particularly influenced by the temperature of the medium (*e.g.* hydrogen abstraction reactions need generally higher activation energies than addition processes), other initiators were used to decrease the temperature of reaction. Performing the induced decomposition of **11** at room temperature (20°C) by using the BEt_3 / O_2 initiating system reported by Brown *et al.* [33] (molar ratio benzene / **11** / BEt_3 = 20 / 1 / 0.1) improved the yield of epoxide **28** (65%). Such behavior confirmed the existence of a secondary reaction of the peroxyketal, favoured by higher temperature.

The result of the induced decomposition of **12** at 110°C was worse than for the reaction of **11** under the same conditions, since the expected ethyl 2-benzyl-2,3-epoxybutanoate **29** was not detected. The presence of methyl benzoate was observed and high-boiling products of reaction were mainly identified as oligomers. The use of AIBN at 80°C for 12 hours does not afford the total decomposition of the starting material (50% of **12** was recovered unchanged) but the formation of methyl benzoate was detected in non-negligible amounts anyway. Similar results were obtained in the case of **13** under the same reaction conditions. A very short chain radical reaction, presumably due to the formation of persistent radicals and the occurence of termination reactions, could explain the remaining peroxyketal. In order to determine the proportion of methyl benzoate

formed either by dihydrogen elimination or by ketalic hydrogen transfer, peroxyketal **12** was heated for 12 hours at 80°C in benzene without initiator. GC analysis exhibited low amounts of methyl benzoate. Its presence would seem to indicate the major occurrence of the radical ketalic hydrogen abstraction at 80°C. The BEt_3 / O_2 initiating system was also used for the induced decomposition of **12** at 20°C in benzene. However, contrary to peroxyketal **11**, the total induced decomposition of **12** was only afforded by the use of an equimolar amount of **12** and BEt_3. Methyl benzoate, benzaldehyde and ethyl adduct **18** were then detected respectively in 64, 18 and 48% yields. The addition of an ethyl radical (issued from BEt_3 autoxidation) on **12** afforded the ethyl adduct **18** and the persistant methoxyphenylmethoxyl radical. Such a radical could evolve either by β-scission, to yield a phenyl radical and methyl formate, or by hydrogen transfer, yielding equivalent amounts of benzaldehyde and methanol from the degradation of the intermediate, unstable hemiketal. The formation of the phenyl adduct **29** has not been observed. The strength of the involved C-C bond (*ca.* 390 $kJ.mol^{-1}$) appears high enough to disfavour the fragmentation process. The absence of similar amounts of benzaldehyde and **18** could be due to the ease of aldehydic hydrogen abstraction[34]. Peroxyketal **12** was also inductively decomposed in cyclohexane to disfavour the possibilities of hydrogen transfer to the peroxyketal itself. In that case, the formation of **19** was observed.

Hydrogen abstraction from the solvent by the oxyl radicals. The reaction of hydrogen abstraction by oxygen-centered radicals from substrate RH (Fig. 1) to generate the expected radical R• is not always selective[2], depending not only on the nature of the hydrogen bonded to the solvent but also to the peroxide (presence of labile hydrogen). The need for a large excess of RH, commonly used as a solvent, to compete with the hydrogen transfer to the peroxidic compound itself, limits severely the field of application of this reaction. In order to improve the yield of glycidic esters in limited amounts of solvents, peroxide **16** and peroxysilane **17**, bearing two methyl fragments in allylic positions, were heated 12 hours in cyclohexane in the presence of **36** as initiator, under conditions similar to those previously reported for the induced decomposition of the corresponding monomethylated peroxide **9** and peroxysilane[2]. However, even in the absence of allylic hydrogens, the yields of **27** (74 and 76%, respectively) were only slightly higher than those of **19** obtained in a previous study (72 and 74%, respectively)[2]. The decrease of the thermal stability of these peroxyderivatives, due to steric compression of the O-O bond, could explain that the yields are not significantly increased.

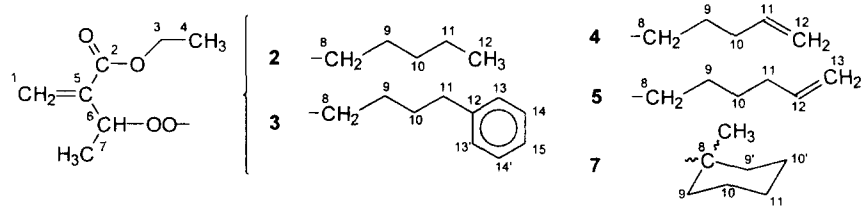
EXPERIMENTAL

General details. ^1H and ^{13}C NMR data were recorded on Hitachi-Perkin-Elmer R 24B (^1H: 60 MHz; CCl_4) or Bruker AC 250 (^1H: 250 MHz, ^{13}C: 69 MHz; $CDCl_3$) spectrometers for 10% solutions of the substances in the solvents. Chemical shifts are reported relative to tetramethylsilane. ^1H and ^{13}C NMR chemical shifts of major diastereoisomer(s) are in bold typeface (when known). Gas chromatographic (GC) analyses were performed with silica capillary columns DB 1 and BP 20 (25 m by 0.25 mm). Flash column chromatographic purifications of peroxidic compounds were carried out on SDS silica gel (200-400 mesh) and monitored by thin layer chromatography (TLC) using Merck precoated silica gel 60 F-254 (0.25 mm thickness) aluminium-backed plates. The plates were visualized under UV or iodine vapor. Retention factor R_f (on TLC) for mixtures of Et_2O and light petroleum ethers (bp = 45-55°C) used as eluent, are mentioned for each peroxidic compound. The purification of oxiranes was performed by a bulb-to-bulb distillation under reduced pressure using a Büchi Kugelrohr oven. Elemental analyses were performed at the Laboratoire Central de Microanalyse (CNRS), Vernaison, France. Analyses of the compounds gave satisfactory agreements between calculated and experimental values with gaps lower than 0.5 % for carbon, hydrogen and oxygen. Cyclohexane and benzene were reagent grade and dried over sodium prior to use whereas dimethyl malonate was distilled and stored over molecular sieves 4 Å. α,α'-Azobis(isobutyronitrile) (AIBN) was obtained from Fluka and recrystallized from methanol. All other reagents were purchased from Aldrich, and used without further purification. *t*-Butyl

peracetate **36** was prepared from *t*-butyl hydroperoxide and acetyl chloride, under basic conditions, as described elsewhere[35]. Triethylborane was available as a 1 M solution in hexane but it was used as 0.1 M solution in a degassed mixture of benzene/hexane (10/1). Cyclohexyl hydroperoxide, 1-hydroperoxy-4-phenylbutane and 1-hydroperoxypentane were prepared according to Williams and Mosher[36,37]. 5-Hydroperoxy pent-1-ene and 6-hydroperoxyhex-1-ene were obtained from Surzur *et al.*[28]. 2,3-Dimethyl-2-hydroperoxybut-3-ene was prepared by photooxygenation of 2,3-dimethyl-2-butene[38]. 1-Hydroperoxy-1-methylcyclohexane was obtained from 1-methylcyclohexanol, following the procedure developped by Milas *et al.*[39]. Hydroperoxides **1** and **15** were similarly obtained from the method developed by Adam and Griesbeck[13]. Access to peroxide **9**, peroxyketal **14**, and oxiranes **19-21** and **27** was reported in previous papers[2,4].

Products stability. The thermal stability of peroxidic compounds similar to those studied in the present article was studied in previous papers[6]. They can be considered as thermally stable under the usual conditions of reaction. Regarding the presence of high-boiling products from the induced decomposition of most of the peroxyderivatives studied, the effect of heating representative epoxides (**22**, **25**, and **27**) in benzene (molar ratio epoxide/benzene = 20/1) was studied at 110°C for 12 hours but no decomposition or isomerization occured.

Synthesis. *Peroxides* ***2-8****: General procedure (method A).* A solution of ethyl 2-bromomethylbut-2-enoate[10] (20.7 g, 0.1 mol), *t*-butyl hydroperoxide, 90% pure (11.0 g, 0.11 mol) and poly(ethylene oxide) (POE 400, 1 g) in tetrahydrofuran (100 cm^3) was vigorously stirred at -10°C. Small portions of powdered KOH, 85% pure (7.25 g, 0.11 mol) were added slowly over 1 h. Stirring was continued for 2 h, the reaction mixture being allowed to warm to room temperature. The solvent was evaporated under vacuum and water (10 cm^3) is added to the residue. The mixture is then extracted three times with distilled light petroleum (30 cm^3), washed with a saturated aqueous NaCl solution and the combined organic layers dried over $MgSO_4$. After elimination of the volatiles in *vacuo*, the residue was purified by flash chromatography on silica gel (*ca.* 100 g). Subjective NMR peak assigments, derived from DEPT experiments, are given on the following chart for peroxides **2-5**, **7**.



Peroxides ***7, 9, and 17****: General procedure (method B).* Alkyl trichloroacetimidate (*t*-butyl: 5.46 g, 1-methylcyclohexyl: 6.46 g, 25 mmol) was prepared according to the literature method[12], and mixed with the hydroperoxide (**1**: 3.52 g, **15**: 3.78 g, 22 mmol) in light petroleum (30 mL) at -10°C, under inert atmosphere. A catalytic amount of BF_3 / Et_2O was then added slowly with a syringe, the reaction mixture being stirred continously for 30 min at -5°C and allowed to warm at room temperature. The precipitated trichloroacetamide was filtered off, solid $NaHCO_3$ (1.0 g) was added to the organic phase and the solvent evaporated. The peroxide was purified by column chromatography on silica gel (*ca.* 80 g).

Ethyl 3-pentyldioxy-2-methylenebutanoate ***2****.* (method A: 9.87 g, 43%); R_f = 0.48, light petroleum-Et_2O = 95 : 5; δ_H ($CDCl_3$) 6.22 (m, 1H), 5.81 (m, 1H) [CH_2=C], 4.91 (q, *J* 6.5, 1H, CH_3CH), 4.14 (q, *J* 7.1, 2H, CO_2CH_2), 3.97 and 3.88 (t, *J* 6.6, 2H, $OOCH_2$), 1.3-1.1 (m, 4H, $OOCH_2(CH_2)_2$), 1.23 (d, *J* 6.5, 3H, CH_3CH), 1.22 (t, *J* 7.1, 3H, $CO_2CH_2CH_3$), 0.80 (bt, 3H, CH_2CH_3); δ_C 165.8 C^2, 141.1 C^5, 124.8 C^1, 76.5 C^6, 74.3 C^8, 60.5 C^3, 28.1 and 27.4 $C^{9,10}$, 22.4 C^{11}, 18.8 C^7, 14.0 C^4, 13.8 C^{12} (Found: C, 62.12; H, 9.76. $C_{12}H_{22}O_4$ requires C, 62.58; H, 9.63 %).

Ethyl 3-(4-phenylbutyl)dioxy-2-methylenebutanoate ***3***. (method A: 13.14 g, 45%); R_f = 0.36, light petroleum-Et_2O = 95 : 5; δ_H ($CDCl_3$) 7.33-7.16 (m, 5H, C_6H_5), 6.36 (m, 1H), 5.94 (m, 1H) [CH_2=C], 4.91 (q, *J* 6.6, 1H, CH_3CH), 4.24 (q, *J* 7.1, 2H, CO_2CH_2), 4.04 (t, *J* 6.6, 2H, $OOCH_2$), 2.65 (t, *J* 7.2, 2H, CH_2Ph), 1.78-1.60 (m, 4H, $(CH_2)_2CH_2Ph$), 1.36 (d, *J* 6.6, 3H, CH_3CH), 1.32 (t, *J* 7.1, 3H, $CO_2CH_2CH_3$); δ_C 165.9 C^2, 142.2 C^{12}, 141.2 C^5, 128.4 and 128.3 $C^{13,13',14,14'}$, 125.8 C^{15}, 125.1 C^1, 76.7 C^6, 74.2 C^8, 60.7 C^3, 35.7 C^{11}, 28.0 and 27.5 $C^{9,10}$; 19.0 C^7, 14.2 C^4 (Found: C, 69.57; H, 8.42. $C_{17}H_{24}O_4$ requires C, 69.83; H, 8.27 %).

Ethyl 3-(pent-4-enyl)dioxy-2-methylenebutanoate ***4***. (method A: 10.72 g, 47%); R_f = 0.43, light petroleum-Et_2O = 95 : 5; δ_H ($CDCl_3$) 6.26 (m, 1H), 5.85 (m, 1H) [CH_2=C], 5.82-5.65 (m, 1H, CH=CH_2), 5.0-4.9 (m, 3H, CH=CH_2, CH_3CH), 4.17 (q, *J* 7.1, 2H, CO_2CH_2), 3.93 (t, *J* 6.5, 2H, $OOCH_2$), 2.05 (bq, 2H, CH_2CH=CH_2), 1.63 (quint, 2H, $OOCH_2CH_2$), 1.26 (d, *J* 6.2, 3H, CH_3CH), 1.25 (t, *J* 7.1, 3H, $CO_2CH_2CH_3$); δ_C 165.8 C^2, 141.1 C^5, 137.8 C^{11}, 125.0 C^1, 115.0 C^{12}, 76.6 C^6, 73.6 C^8, 60.6 C^3, 30.1 C^{10}, 26.9 C^9, 18.9 C^7, 14.1 C^4 (Found: C, 63.06; H, 8.76. $C_{12}H_{20}O_4$ requires C, 63.13; H, 8.83 %).

Ethyl 3-(hex-5-enyl)dioxy-2-methylenebutanoate ***5***. (method A: 10.89 g, 45%); R_f = 0.43, light petroleum-Et_2O = 95 : 5; δ_H ($CDCl_3$) 6.23 (m, 1H), 5.82 (m, 1H) [C^1H_2=C], 5.79-5.62 (m, 1H, CH=CH_2), 4.95-4.84 (m, 3H, CH=CH_2, CH_3CH), 4.14 (q, *J* 7.1, 2H, CO_2CH_2), 3.90 (t, *J* 6.5, 2H, $OOCH_2$), 1.98 (br q, 2H, CH_2CH=CH_2), 1.58-1.29 (m, 4H, $C^9H_2C^{10}H_2$), 1.25-1.20 (m, 6H, CH_3CH and $CO_2CH_2CH_3$); δ_C 165.8 C^2, 141.1 C^5, 138.3 C^{12}, 124.9 C^1, 114.6 C^{13}, 76.6 C^6, 74.1 C^8, 60.5 C^3, 33.4 C^{11}, 27.2 C^9, 25.3 C^{10}, 18.9 C^7, 14.1 C^4 (Found: C, 64.18; H, 8.93. $C_{13}H_{22}O_4$ requires C, 64.44; H, 9.15 %).

Ethyl 3-(1-methylcyclohexyl)dioxy-2-methylenebutanoate ***7***. (method A: 6.65 g, 26% and B: 1.97 g, 35%); R_f = 0.50, light petroleum-Et_2O = 95 : 5; δ_H ($CDCl_3$) 6.12 (m, 1H), 5.85 (m, 1H) [CH_2=C], 4.83 (q, *J* 6.5, 3H, CH_3CH), 4.14 (q, *J* 7.6, 2H, CO_2CH_2), 1.65-1.20 (m, 16H, cyclic CH_2, CH_3CH and $CO_2CH_2CH_3$), 1.15 (s, 3H, C-CH_3); δ_C 165.9 C^2, 141.1 C^5, 124.7 C^1, 80.8 C^8, 77.1 C^6, 60.4 C^3, 35.1 and 34.9 $C^{9,9'}$, 25.7 C^{11}, 24.4 C^{12}, 22.3 and 22.2 $C^{10,10'}$, 18.8 C^7, 14.1 C^4 (Found: C, 65.62; H, 9.50. $C_{14}H_{24}O_4$ requires C, 65.60; H, 9.44 %).

Ethyl 3-(1,1-dimethylpropen-2-yl)dioxy-2-methylenebutanoate ***8***. (method A: 2.63 g, 30%); R_f = 0.53, light petroleum-Et_2O = 97 : 3; δ_H (CCl_4) 6.2 (s, 1H), 5.9 (s, 1H), 5.0 (s, 1H), 4.7 (s, 1H) [2 × CH_2=C], 4.8 (q, *J* 6.5, 1H, CH_3CH), 4.1 (q, *J* 7.5, 2H, CO_2CH_2), 1.75 (s, 3H, CH_3-C=), 1.3-1.1 (m, 12H, $(CH_3)_2C$, CH_3CH and $CO_2CH_2CH_3$).

Ethyl 3-t-butyldioxy-2-methylenebutanoate ***9***. (method B: 6.74 g, 78%); R_f = 0.40, light petroleum-Et_2O = 97 : 3. The preparation of this material by the method A and its spectroscopic analysis are described elsewhere[2].

Ethyl 3-acetyldioxy-2-methylenebutanoate ***10***. This perester can be prepared by a general method described by Milas and Surgenor[21]. To a stirred solution of pyridine (1.58 g, 0,02 mol) in light petroleum (10 cm^3), acetyl chloride (1.57 g, 0.02 mol) was added dropwise. The stirred reaction mixture was then cooled to -10°C and a solution of **1** (3.20 g, 0.02 mol) in light petroleum (5 cm^3) was added dropwise to the medium. This was then allowed to warm slowly to room temperature over 30 min after which it was filtered. The organic layer was washed with brine (10 cm^3) and dried over anhydrous magnesium sulfate. The solvent was evaporated in vacuo and the perester purified by flash chromatography on silica gel (60 g) to yield **10** as a colorless liquid (1.29 g, 32%); R_f = 0.47, light petroleum-Et_2O = 85 : 15; δ_H (60 MHz, CCl_4) 6.2 (s, 1H), 5.9 (s, 1H) [CH_2=C], 5.05 (q, *J* 7.0, 3H, CH_3CH), 4.15 (q, *J* 7.0, 2H, CO_2CH_2), 1.95 (s, 3H, $COCH_3$), 1.4 (d, *J* 7.0, 3H, CH_3CH), 1.3 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$); (Found: C, 53.40; H, 7.02. $C_9H_{14}O_5$ requires C, 53.46; H, 6.98 %).

Ethyl 3-(1-methoxyhex-2-enyl)dioxy-2-methylenebutanoate ***11***. (2.12 g, 78%); R_f = 0.42, light petroleum-Et_2O = 90 : 10; δ_H (CCl_4) 6.05-5.45 (m, 4H, CH_2=C, CH=CH), 5.2 (m, 1H, O-CH-O), 4.85 (q, *J* 6.0, 3H, CH_3CH), 4.15 (q, *J* 7.5, 2H, CO_2CH_2), 3.30 (s, 3H, OCH_3), 2.0-0.8 (m, 13H); (Found: C, 61.65; H, 8.97. $C_{14}H_{24}O_5$ requires C, 61.74; H, 8.88 %).

Ethyl 3-methoxyphenylmethyldioxy-3-methylenebutanoate ***12***. (4.11 g, 73%); R_f = 0.35, light petroleum-Et_2O = 85 : 15; δ_H (CCl_4) 7.3-7.0 (m, 5H, C_6H_5), 6.1 (s, 1H), 5.7 (s, 1H) [CH_2=C], 5.6 (s, 1H, O-CH-O), 4.8 (q, *J* 7.0, 3H, CH_3CH), 4.2 (q, *J* 7.5, 2H, CO_2CH_2), 3.5 (s, 3H, OCH_3), 1.5-1.2 (m, 6H, CH_3CH and $CO_2CH_2CH_3$).

Ethyl 3-methoxyfurfurylmethyldioxy-2-methylenebutanoate ***13***. (3.26 g, 60%); R_f = 0.31, light petroleum-Et_2O = 85 : 15; δ_H (CCl_4) 7.1 (bs, 1H), 6.1 (bs, 2H) [cycle], 6.0 (s, 1H), 5.7 (s, 1H) [CH_2=C], 5.5 (s, 1H, O-CH-O), 4.8 (q, *J* 7.0, 3H, CH_3CH), 4.0 (q, *J* 7.0, 2H, CO_2CH_2), 3.3 (s, 3H, OCH_3), 1.5-1.1 (m, 6H, $CO_2CH_2CH_3$ and CH_3CH).

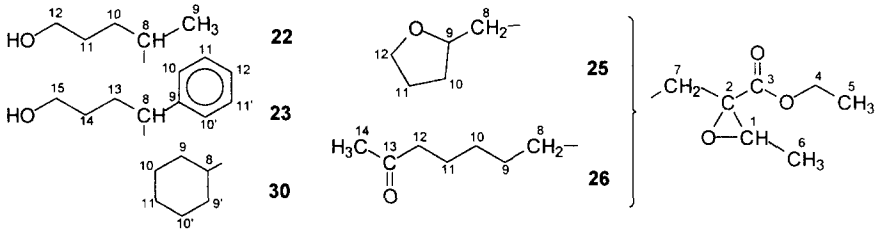
Ethyl 3-hydroperoxy-3-methyl-2-methylenebutanoate ***15***[13]. (17.4 g, 100%); δ_H (CCl_4) 9.0 (s, 1H, OOH), 6.3 (m, 1H), 5.9 (m, 1H) [CH_2=C], 4.2 (q, *J* 7.1, 2H, CO_2CH_2), 1.3 (s, 6H, $(CH_3)_2C$), 1.2 (t, *J* 7.1, 3H, $CO_2CH_2CH_3$).

Ethyl 3-trimethylsilyldioxy-3-methyl-2-methylenebutanoate ***16***. It was prepared by dropwise addition of trimethylsilyl chloride (2.17 g, 0.02 mole) to a stirred solution of pyridine (1.58 g, 0.02 mole) in anhydrous heptane (20 cm^3), cooled to 0°C. The stirred reaction mixture was then cooled to -10°C and a solution of ethyl 3-hydroperoxy-3-methyl-2-methylenebutanoate **15** (3.48 g, 0.02 mole) in heptane (5 cm^3) was added dropwise. The mixture was then allowed to warm slowly to room temperature and filtered. The organic layer was quickly washed with water (20 cm^3) and dried ($MgSO_4$). The solvent was evaporated under vaccuum and the residue was bulb-to-bulb distilled to afford **16** as a colorless liquid (4.68 g, 95 %), $bp_{0.1}$ = 60°C; δ_H (CCl_4) 6.4 (m, 1H), 5.9 (m, 1H) [CH_2=C], 4.2 (q, *J* 7.0, 2H, CO_2CH_2), 1.3 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$), 1.2 (2s, 6H, $(H_3C)_2C$), 0.2 (s, 9H, $Si(CH_3)_3$); (Found: C, 53.49; H, 8.92. $C_{11}H_{22}O_4Si$ required C, 53.63; H, 9.00 %).

Ethyl 3-tert-butyldioxy-3-methyl-2-methylenebutanoate ***17***. (method B: 3.24 g, 47 %); R_f = 0.38, light petroleum-Et_2O = 97 : 3; δ_H (CCl_4) 6.25 (m, 1H), 5.85 (m, 1H) [CH_2=C], 4.20 (q, *J* 7.0, 2H, CO_2CH_2), 1.33 (sd, 6H, $(CH_3)_2C$), 1.27 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$), 1.15 (s, 3H, $C(CH_3)_3$); (Found: C, 62.51; H, 9.69. $C_{12}H_{22}O_4$ requires C, 62.58; H, 9.63 %).

General procedure for the induced decomposition of peroxydic compounds.

A mixture of a peroxydic compound (20 mmol) and an initiator (2 mmol, **36**: 0.26 g, AIBN: 0.33 g) was added to a glass tube containing the amount of solvent (200 mmol; benzene: 15.6 g, cyclohexane: 16.8 g, dimethyl malonate: 26.4 g) required to produce a molar ratio solvent / peroxyderivative / initiator equal to 20 / 1 / 0.1. The tube was sealed under reduced pressure (10^{-3} Torr) and heated 12 h (**36**: 110°C, AIBN: 80°C). The volatiles were then removed under vacuum and the glycidic ester was distilled with a bulb-to-bulb apparatus. Subjective NMR peak assigments, derived from DEPT experiments, are given on the following chart for epoxides **22**, **23**, **25**, **26** and **30**.



Ethyl 2,3-epoxy-2-(2-methyl-5-hydroxypentyl)butanoate ***22***. $bp_{0.01}$ = 120°C; δ_H ($CDCl_3$) 4.1-3.9 (m, 2H, CO_2CH_2), 3.35 (bt, 2H, $HOCH_2$), 3.1 (s, 1H, OH), **3.0** and 2.8 (q, *J* 5.5, 1H, $CHCH_3$), 2.2-1.2 (m, 7H, $CH_2CH_2CHCH_2$), 1.15 (d, *J* 5.5, 3H, $CHCH_3$), 1.1 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$); δ_C **171.3 171.2** 169.8 169.6 C^3, **62.4 62.3** C^{12}, **61.2** 61.1 C^4, 60.4 60.2 C^2, 58.6 **57.5** 57.4 **56.8** C^1, **33.8 33.4** C^7, **33.3 32.6** C^{11}, 30.5 **30.3 30.0**

C^8, 29.8 **29.7** 29.6 C^{10}, **19.6** C^9, 14.1 **13.9** C^6, **13.6** 13.5 **13.4** C^8 (Found: C, 62.51; H, 9.72; $C_{12}H_{22}O_4$ required C, 62.58; H, 9.63 %).

Ethyl 2,3-epoxy-2-(2-phenyl-5-hydroxypentyl)butanoate ***23***. $bp_{0.01}$ = 150°C; δ_H ($CDCl_3$) 7.26-6.97 (m, 5H, C_6H_5), 4.04 (q, *J* 7.2, 2H, CO_2CH_2), 3.41 (t, *J* 6.4, 2H, $HOCH_2$), **3.06** and 3.00 (q, *J* 5.4, 1H, $CHCH_3$), 2.92-2.72 (m, 1H, C*H*Ph), 2.55 (s, 1H, OH), 2.51-2.32 (m, 2H, C^7H_2), 2.2-1.5 (m, 4H, $^{13}CH_2{}^{12}CH_2$), 1.4-1.0 (m 6H, $CO_2CH_2CH_3$); δ_C **171.2 170.9** 169.8 169.4 C^3, 144.1 143.7 C^9, **128.3 128.2 128.1 127.7** $C^{10,10',11,11'}$, 126.4 **126.3** C^{12}, 62.3 62.2 C^{12}, **61.4 61.2** 61.1 C^4, 60.2 59.9 C^2, 59.7 58.5 57.7 C^1, 42.4 42.3 C^8, 34.5 34.1 C^7, 32.6 32.1 32.0 C^{14}, 30.6 30.5 C^{13}, **14.1** 13.9 13.7 C^6, **13.6** 13.5 C^5 (Found: C, 69.77; H, 8.34; $C_{17}H_{24}O_4$ required C, 69.84; H, 8.27 %).

Methyl (6,7-epoxy-6-ethoxycarbonyl-4-methyl)octyl malonate ***24***. $bp_{0.01}$ = 170°C; δ_H ($CDCl_3$) 4.1-3.9 (m, 4H, 2 × CO_2CH_2), 3.55 (s, 3H, OCH_3), 3.2 (s, 2H, CH_2), **3.0** and 2.8 (q, *J* 5.5, 1H, $CHCH_3$), 2.2-1.2 (m, 7H, $(CH_2)CHCH_2$), 1.15 (d, *J* 5.5, 3H, $CHCH_3$), 1.1 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$).

Ethyl 2,3-epoxy-2-(2-tetrahydrofuran-2-ylethyl)butanoate ***25***. $bp_{0.2}$ = 80°C; δ_H ($CDCl_3$) 4.08-3.89 (m, 2H, CO_2CH_2), 3.86-3.58 (m, 2H, $C^{12}H_2$), 3.53-3.45 (m, 2H, C^9H_2), **3.06** (q, *J* 5.5, 1H, $CHCH_3$), 2.2-1.13 (m, 8H, other CH_2), 1.16 (d, *J* 5.5, 3H, $CHCH_3$), 1.07 (t, *J* 7.1, 3H, $CO_2CH_2CH_3$); δ_C **170.7** 169.2 C^3, **78.6 78.5** 78.4 78.3 C^9, 68.1 68.0 **67.4 67.3** C^{12}, 61.3 **61.2** 61.1 C^4, 60.6 60.5 C^2, 58.4 58.3 **58.1 58.0** C^1, **31.0** C^{11}, 31.1 30.9 C^{10}, 25.6 25.5 25.2 C^8, 24.4 24.1 C^9, 14.1 **13.9** C^6, 13.6 **13.5 13.4** C^8 (Found: C, 63.24; H, 8.66; $C_{12}H_{20}O_4$ required C, 63.14; H, 8.83 %).

Ethyl 2,3-epoxy-2-(7-oxooctyl)butanoate ***26***. $bp_{0.01}$ = 120°C; δ_H ($CDCl_3$) 4.07-3.88 (m, 2H, CO_2CH_2), **3.02** and 2.84 (q, *J* 5.4, 1H, $CHCH_3$), 2.22 (t, *J* 7.3, 2H, $COCH_2$), 1.91 (s, 3H, CH_3CO), 1.41-1.19 (m, 10H, other CH_2), 1.13 (d, *J* 5.4, 3H, $CHCH_3$), 1.06 (t, *J* 7.1, 3H, $CO_2CH_2CH_3$); δ_C **170.6** 169.3 C^3, 168.2 C^{13}, 62.9 **60.5** C^2, **60.9** 60.8 C^4, 58.0 **57.7** C^1, 43.1 C^{12}, 29.4 C^{14}, 32.6 **29.0** C^7, 28.7 **28.5** 26.9 24.6 24.2 **23.2** $C^{8,9,10,11}$, 13.9 **13.7** C^6, 13.3 **13.2** C^5 (Found: C, 65.54; H, 9.38; $C_{14}H_{24}O_4$ required C, 65.60; H, 9.44 %).

Ethyl 2,3-epoxy-2-(hex-2-enyl)butanoate ***28***. To a vigorously stirred solution of peroxyketal **11** (2.72 g, 10 mmol) in benzene (10 cm^3) was added dropwise a 0.1 M solution of triethylborane in benzene/hexane (10 cm^3) over 30 min at 20°C. Air bubbling was continuously added to the medium during the whole reaction time. The absence of remaining **11** was controlled by GC analysis. Solvents were then removed in vacuo (10^{-2} Torr) and **28** distilled as a colorless liquid (1.38 g, 65%); $bp_{0.01}$ = 75°C; δ_H (CCl_4) 5.85-5.20 (m, 2H, CH=CH), 4.1-3.85 (m, 2H, CO_2CH_2), **3.0** and 2.85 (bq, 1H, $CHCH_3$), 1.4-1.2 (m, 6H, CH_2), 1.15 (bd, 3H, $CHCH_3$), 1.1-0.9 (m, 6H, $CO_2CH_2CH_3$ and CH_3CH_2).

Ethyl 2-cyclohexylmethyl-2,3-epoxy-3-methylbutanoate ***30***. $bp_{0.1}$ = 100°C; δ_H 4.20 ($CDCl_3$) (m, 2H, CO_2CH_2), 2.1-0.8 (m, 22H); δ_C 171.4 C^3, 61.1 C^4, 58.0 C^2, 52.5 C^1, 35.0 C^8, 34.0 C^7, 33.3 33.2 $C^{9,9'}$, 26.1 26.0 $C^{10,10'}$, 25.8 C^{11}, 21.5 21.0 $C^{6,6'}$, 13.9 C^5; (Found: C, 70.09; H, 9.94; $C_{14}H_{24}O_3$ required C, 69.96; H, 10.07 %).

Ethyl 2,3-epoxy-2-(1-imidazolylmethyl)butanoate ***31***. This compound was obtained from the reaction of ethyl 3-hydroperoxy-2-methylenebutanoate **1**, acetyl chloride and *N,N'*-carbonyldiimidazole in anhydrous THF at 0°C, according to the procedure reported by Rüchardt and coll.[19]; $bp_{0.3}$ = 95-100°C; δ_H (60 MHz, D_6-acetone) 7.6 (s, 1H, N=CH-N), 6.9 (s, 2H, CH=CH), 3.95 (q, *J* 7.0, 2H, CO_2CH_2), 3.2 (q, *J* 7.0, 1H, CH_3CH), 3-1.9 (m, 2H, N-CH_2), 1.1 (d, *J* 7.0, 3H, $CHCH_3$), 1,0 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$) (Found: C, 57.05; H, 6.78; O, 22,97. $C_{10}H_{14}N_2O_3$ requires C, 57.13; H, 6.71; O, 22.83 %).

Reaction of hydroperoxide 1 and silylated enol ether. A solution of **1** (4.80 g, 30 mmol) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) in Et_2O (50 cm^3) was cooled with stirring to -10°C. To the cooled solution was added dropwise a solution of 3-trimethylsilyl-2-oxa-1-butene (2.64 g, 30 mmol) in Et_2O (10 cm^3). The stirred reaction mixture was then allowed to warm to room temperature and was washed with an aqueous solution of Na_2CO_3 (10 cm^3) and water (2 × 10 cm^3). The combined organic layers were dried over

anhydrous $MgSO_4$. The solvent was removed under reduced pressure (10^{-2} Torr) and the crude product was purified by flash chromatography on a column of silica gel (80 g). Two major products were isolated and identified, the alcohol **34**[40] (0.86 g, 20%) and ethyl 3-acetyloxy-2-methylenebutanoate **35**[9] (1.95 g, 35%); δ_H (CCl_4) 6.15 (m, 1H) and 5.70 (m, 1H) [CH_2=C], 5.55 (q, *J* 7.0, 1H, C*H*CH_3), 4.15 (q, *J* 7.0, 2H, CO_2CH_2), 2.0 (s, 3H, $COCH_3$), 1.35 (d, *J* 7.0, 3H, CHC*H*$_3$), 1.30 (t, *J* 7.0, 3H, $CO_2CH_2CH_3$).

CONCLUSION

Various alkyl radicals have been generated from oxyl radicals via inter- or intramolecular hydrogen transfer, cyclization or fragmentation, this latter case leading to one or two entities. It appears that a thorough knowledge of the reactivity of the oxyl radicals in solution is needed to produce efficiently and selectively the alkyl radicals required. These alkyl radicals have promoted the induced decomposition of several methacrylic-type peroxyderivatives, yielding substituted oxiranes in good to high yields. Dihydrogen elimination and ketalic hydrogen transfer processes seem to be involved in the thermal degradation of secondary peroxyderivatives to various extend. It was shown previously that the presence of an alkylalkoxymethyl group on the peroxy function favours the dihydrogen elimination as the main side-reaction[4]. In the present study, the presence of an olefinic or an aryl group on the acetalic fragment seems to favour the acetalic hydrogen transfer as the major homolytic degradation reaction.

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REFERENCES

1. Navarro, C.; Degueil-Castaing, M.; Colombani, D.; Maillard, B. *Synlett* **1992**, 587-588.
2. Colombani, D.; Maillard, B. *J. Chem. Soc., Perkin Trans 2* **1994**, 745-752.
3. Colombani, D.; Maillard, B. *J. Chem. Soc, Chem. Commun.* **1994**, 1259-1260.
4. Colombani, D.; Maillard, B. *J. Org. Chem.* **1994**, *59*, 4765-4772.
5. Colombani, D.; Chaumont, P. *Progr. Polym. Sci.* **1996**, *21*, 439-503.
6. a) Colombani, D.; Zink, M.O.; Chaumont, P. *Macromolecules* **1996**, *29*, 819-825.
   b) Colombani, D.; Chaumont, P. *Polymer* **1995**, *36*, 129-135.
   c) Colombani, D.; Chaumont, P. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2687-2693.
   d) Colombani, D.; Chaumont, P. *Macromolecules* **1994**, *27*, 5972-5978.
7. a) Vertommen, L.L.T., Meijer, J.; Maillard, B.J. *PCT Int. Appl.* WO 9107,387 (1991); *Chem. Abstr.* **1991**, *115*, 160039q. b) Meijs, G.F.; Rizzardo, E.; Thang, S.H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*(1), 893.
8. Colombani, D., Maillard, B. *Tetrahedron* **1996**, *52*, 14855-14864.
9. Navarro, C.; Degueil-Castaing, M.; Colombani, D.; Maillard, B. *Synth. Commun.* **1993**, *23*, 1025-1037.
10. Ameer, F.; Drewes, S.E.; Emslie, N.D.; Kaye, P.T.; Mann, R.L. *J. Chem. Soc., Perkin Trans 1* **1983**, 2293-2295.
11. Davies, A.G.; Foster, R.V.; White, A.M. *J. Chem. Soc.* **1953**, 1541-1547.
12. a) Bourgeois, M.J.; Maillard, B.; Montaudon, E. *Tetrahedron* **1993**, 49, 2477-2484.
    b) Armstrong, A.; Brackenridge, I.; Jackson, R.F.W.; Kirk, J.M. *Tetrahedron Lett.* **1988**, *29*, 2483-2486.
13. Adam, W.; Griesbeck, A. *Synthesis* **1986**, 1050-1052.

14. Sum, F.W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431-1441.
15. Silbert, L.S.; Swern, D. *Anal. Chem.* **1958**, *30*, 385-387.
16. a) Buncel, E.; Davies, A.G. *Chem. and Ind.* **1956**, 1052-1053.
b) Buncel, E.; Davies, A.G. *J. Chem. Soc.* **1958**, 1550-1556.
17. Harmon, D. *US Pat.* 2 608 570 (1952); *Chem. Abstr.* **1954**, *48*, 3387a.
18. Greene, F.D.; Kazan, J. *J. Org. Chem.* **1963**, *28*, 2168-2171.
19. a) Hecht, R.; Rüchardt, C. *Chem. Ber.* **1963**, *96*, 1281-1284.
b) Staab, H.A.; Rohr, W.; Graf, F. *Chem. Ber.* **1965**, *98*, 1122-1127.
20. Montaudon, E.; Campagnole, M., Bourgeois, M.J.; Maillard, B. *Bull. Soc. Chim. Belg.* **1982**, *91*, 725-730.
21. Milas, N.A.; Surgenor, D.M. *J. Am. Chem. Soc.* **1946**, *68*, 642-643.
22. Criegee, R. *Ann.* **1948**, *560*, 127-135.
23. Denney, D.B. *J. Am. Chem. Soc.* **1955**, *77*, 1706-1707.
24. Rieche, A.; Schmitz, E.; Bischoff, C. *Germ. Pat.* 1,083,821 (1960).
25. Langhals, H.; Fisher, H. *Chem. Ber.* **1978**, *111*, 543-553.
26. Walker, J.; Appleyard, J.R. *J. Chem. Soc.* **1895**, *67*, 768-770.
27. March, J. *Advanced Organic Chemistry*, Fourth Ed., Wiley Interscience, p. 397-398 (1992).
28. Taillez, B.; Bertrand, M.P.; Surzur, J.M. *J. Chem. Soc., Perkin Trans 1* **1983**, 547-552.
29. Laird, E.R.; Jørgensen, W.L. *J. Org. Chem.* **1990**, *55*, 9-27.
30. Beckwith, A.L.J. *Tetrahedron* **1981**, *37*, 3073-3100.
31. Surzur, J.M.; Bertrand, M.P.; Nouguier, R. *Tetrahedron Lett.* **1969**, 4150-4197.
32. a) Durham, L.J.; Mosher, H.S. *J. Am. Chem. Soc.* **1960**, *82*, 4537-4542.
b) Durham, L.J.; Wurster, C.F.; Mosher, H.S. *J. Am. Chem. Soc.* **1958**, *80*, 332-337.
33. Brown, H.C.; Midland, M.M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 692-700.
34. Navarro, C.; Saux, A.; Maillard, B. *New. J. Chem.* **1992**, *16*, 993-998.
35. Bartlee, P.D.; Hiatt, R.R. *J. Am. Chem. Soc.* **1958**, *80*, 1398-1405.
36. Williams, H.R.; Mosher, H.S. *J. Am. Chem. Soc.* **1954**, *76*, 2984-2987.
37. Williams, H.R.; Mosher, H.S. *J. Am. Chem. Soc.* **1954**, *76*, 2987-2990.
38. Schenck, G.O.; Schulte-Elte, K.H. *Justus Liebigs Ann. Chem.* **1958**, *618*, 185-193.
39. Milas, N.A.; Perry, L.H. *J. Am. Chem. Soc.* **1946**, *68*, 1938-1940.
40. Fikentscher, R.; Hahn, E.; Kud, A.; Oftring, A. *Germ. Pat.* 3,444,098 (1986); *Chem. Abstr.* **1986**, *105*, 115538k.

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