Tetrahedron Vol. 41, No. 19, pp. 4047 to 4056, 1985
Printed in Great Britain

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

INTRAMOLECULAR HOMOLYTIC DISPLACEMENTS 7 - FREE RADICAL ADDITIONS TO UNSATURATED PEROXY COMPOUNDS : SYNTHESIS OF OXYGENATED HETEROCYCLES

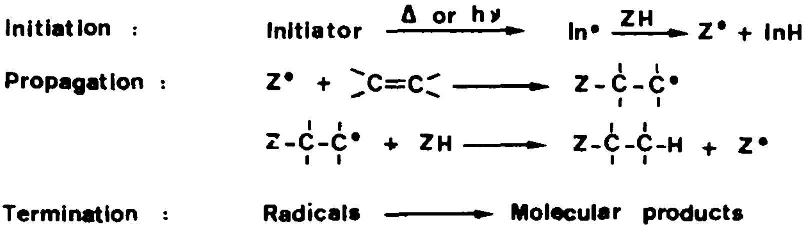
BERNARD MAILLARD[(a)]*, ABDELMAJID KHARRAT[(b)], FELICIEN RAKOTOMANANA[(b)],
EVELYNE MONTAUDON[(b)] and CHRISTIAN GARDRAT[(b,c)]

(a) Laboratoire de Chimie Organique du Silicium et de l'Etain, CNRS, UA 35
(b) Laboratoire de Chimie Appliquée
(c) Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux
Université de Bordeaux I, 351, cours de la Libération 33405 TALENCE-CEDEX,
France.

(*Received in Germany* 31 *January* 1985)

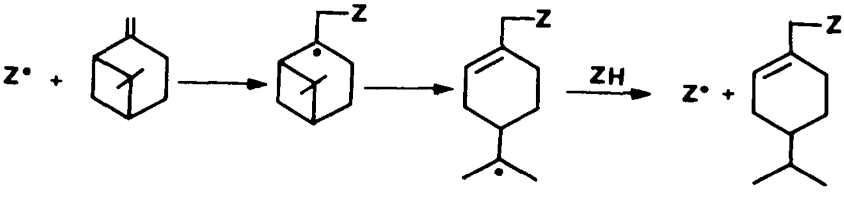
Abstract - Free radical additions of hydrogen donor solvents to tert-butyl perpent-4-enoate have given 4-substituted γ-butyrolactones, with yields of 50 % or greater. Such reactions applied to allyl-tert-butyl peroxide have produced 2,3-epoxypropanation of these solvents. Similar addition-elimination processes occurred with tert-butyl 4-methyl-perpent-4-enoate, tert-butyl 2,2-dimethyl-perpent-4-enoate and tert-butyl-methallyl peroxide, but they failed with tert-butyl 5-methyl-perhex-4-enoate and tert-butyl-3-methyl-but-2-enyl peroxide.

Free radical additions to alkenes have been extensively studied since they are very easy and efficient methods of alkylation of hydrogen donor substrates[1]. They proceed by a chain mechanism (Scheme 1).



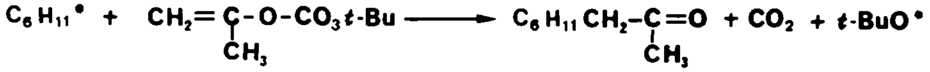
Scheme 1

Homolytic rearrangements following additions to carbon-carbon double bonds have been used to prepare specific compounds. A well-known example of such a reaction sequence occurs in the case of β-pinene (Scheme 2). Various compounds with a p-menthenic skeleton have been obtained in our laboratory[2].



Scheme 2

During the study of the thermal stability of percarbonates, a significant induced decomposition of the O,O-tert-butyl O-isopropenyl percarbonate by cyclohexyl radicals was discovered[3] (Scheme 3).



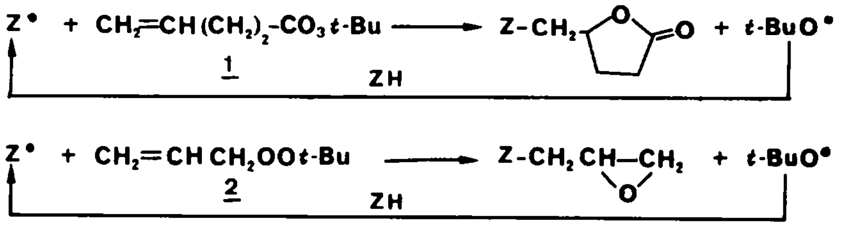
$$C_6H_{11}^\bullet + CH_2{=}\underset{\displaystyle CH_3}{C}{-}O{-}CO_3t\text{-Bu} \longrightarrow C_6H_{11}CH_2{-}\underset{\displaystyle CH_3}{C}{=}O + CO_2 + t\text{-BuO}^\bullet$$

Scheme 3

With the acetonylation of hydrogen donor substrates by such a reaction, investigations were begun on the potential synthetic use of the induced decompositions of unsaturated peroxidic compounds.

As described in Tidwell's review[5], the peroxidic derivatives of acids are used to undergo induced decompositions by intramolecular displacements. Similar homolytic substitutions are involved in γ-elimination of the tert-butoxyl group in β-peroxy radicals[6]. These results prompted us to study the decomposition of tert-butyl perpent-4-enoate (1) and allyl-tert-butyl peroxide (2) in hydrogen donor solvents ZH.

In previous papers[7] we noticed that the thermolysis of 1 in ZH led to the formation of substituted butyrolactones through a two-step addition-elimination reaction[8] (Scheme 4). Similarly, we have showed that heating tert-butyl-allyl peroxide 2 in a cyclic alkane or an ether caused the 2,3-epoxypropanation of these substrates[9a] (Scheme 4). Under such thermal conditions, the peroxidic compounds is consumed by two competitive induced and spontaneous decompositions. Although the homolysis of the O-O bond is necessary to initiate the free radical addition-elimination pathway, it is a material wasting process (indeed, it cannot give any functionalized substrate). An easy way to eliminate such a competition is to generate $Z^\bullet$ under conditions where the unsaturated "peroxides" are thermally stable. This led us to explore homolytic additions of ZH to 1 and 2 using a "low temperature" initiator ; this paper deals with the results of these studies.



Scheme 4

In the first section, the optimal reaction conditions are described. In the second, free radical additions of ZH to 1 and 2 are compared with their thermolyses in the same solvents. In the last section, the synthetic limitations of such addition-elimination reactions using substituted peroxidic compounds are discussed.

DETERMINATION OF THE OPTIMAL REACTION CONDITIONS

Preliminary experiments were performed to optimize several experimental parameters for the free radical additions, namely temperature, duration of the reaction and molar ratios of the reactants.

1°) Tert-butyl perpent-4-enoate 1

Because of the well-known thermal stability of tert-butyl per-n-alcanoates[10], benzoyl peroxide - 24 h, 80°C[11] - or the diperester deriving from 2-N-methylaminoethanol ($t\text{-BuO}_3CN(CH_3)CH_2CH_2OCO_3tBu$) - 32 h, 60°C[12] - were used as initiators.

The optimal molar ratio of alkene/initiator generally lies in the range 5-100[1]. Preliminary experiments, using commercial benzoyl peroxide and tetrahydrofuran or cyclohexane (Table 1) showed that the 1/initiator ratio was optimized at a value of 10. The different ZH model compounds were added to 1 using the best ZH/1 ratio, as determined during the thermolysis[7,8], for each initiator. The results summarized in table 2 indicate that benzoyl peroxide is generally more efficient than the diperester.

Table 1. Influence of 1/benzoyl peroxide molar ratio on the yields of lactones

1/benzoyl peroxide	Yield of lactone (%) (a)  (b)	 (c)
1/0.05	47	48
1/0.1	73	56
1/0.2	57	46

(a) Measured by GC on the reaction mixture relative to the starting 1 (b) Molar ratio cyclohexane/1=50 (c) Molar ratio tetrahydrofuran/1=20.

Table 2. Effect of initiator on the yields of lactones

ZH Conditions	Yield of lactone (%) (a)  (d)	 (e)	$CH_3CH_2CO_2CH_3$ (f)	$CH_3CH_2\underset{O}{\overset{\|}{C}}CH_2CH_3$ (e)	CH_2Cl_2 (d)
Benzoyl peroxide 80°C-12h (b)	73	56	62	48	70
"Diperester" 60°C-32h (b)	54	48	49	69	66
Thermolysis 110°C-8h (c)	24	42	58	33	58

(a) Measured by GC on the reaction mixture relative to the starting 1 (b) Molar ratio 1/initiator=10 (c) Results taken from[7] (d) Molar ratio ZH/1=50 (e) Molar ratio ZH/1=20 (f) Molar ratio ZH/1=100.

An optimal value for ZH/1 can be defined from the results indicated in table 3.

Table 3. Effect of ZH/1 molar ratio on the yields of lactones

ZH/1 ZH	Yield of lactone (%) (a) 		$CH_3\underset{a}{CH_2}CO_2\underset{b}{CH_3}$ (b)	$CH_3CH_2\underset{O}{\overset{\|}{C}}CH_2CH_3$	CH_2Cl_2	CH_3CN
20	52	56	68	48	58	49
50	73	58	71	58	70	64
100	58	65	62	43	51	60

(a) Measured by GC on the reaction mixture relative to the starting 1 with a molar ratio 1/benzoyl peroxide of 10 at 80°C for 24 h (b) Presence of the two lactones resulting of a substitution on the hydrogens *a* and *b* (*a*/*b*=94/6) whatever have been ZH/1.

Thus, the selected conditions of the free radical additions to 1 were found to be a ZH/1/benzoyl peroxide ratio of 50/1/0.1 at 80°C for 24 h.

2°) Allyl tert-butyl peroxide 2

The higher stability of the allyl-tert-butyl peroxide[13] suggests that tert-butyl peresters[10] and acyl peroxides[14] would be good candidates to initiate free radical additions to 2. Since the expected products are epoxides which are well-known to be sensitive towards acids, benzoyl peroxide and perester of benzoic acid are unsuitable initiators because they produce acid when decomposed in hydrogen donor solvents[11,15]. However, the acetoxy radical with its more rapid decarboxylation $-k_{CO_2} = 10^{10} s^{-1}$ at 100°C[16] - suggests that the peroxy derivatives of acetic acid could be used for the initiation, avoiding the formation of acid, even with good hydrogen donors. Unfortunately, acetyl peroxide is recognized as a compound which is unsafe to handle ; this left us to choose between benzoyl peroxide and tert-butyl peracetate. Fewer experiments have been performed with 2 than with 1. The data recorded in table 4 led us to select the experimental conditions of a ZH/2/tert-butyl peracetate molar ratio of 100/1/0.1 at 110°C for 12 h.

Table 4. Influence of the initiator and of ZH/2 molar ratios on the yields of 2,3-epoxypropanation of some model solvents

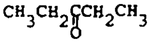
Initiator [(b)] (°C, h)	ZH/2	Yield of epoxide (%) [(a)]		
			$CH_3CH_2CO_2CH_3$	CH_2Cl_2
Tert-butyl peracetate (110°C, 12h)	100/1	70	67	76
	50/1	54	45	49
	20/1	49	48	36
Benzoyl peroxide (80°C, 24h)	100/1	68	63	75

[(a)] Measured by GC on the reaction mixture relative to the starting 2 [(b)] Molar ratio 2/initiator=10

FREE RADICAL ADDITION OF ZH TO 1 AND 2

Table 5 shows the general improvement of the yields in functionalized solvent when the reaction was performed using an initiator. The most significant results were obtaiend with cyclohexane (yields were doubled). We must underline that the yields were always equal to 50 % or greater except in the case of the 2,3-epoxypropanation of acetonitrile.

Table 5. Comparison of the yields of lactones and epoxides from thermolysis of 1 and 2 in ZH and addition to them.

ZH	Yield of pentanolidation (%) [(a)]		Yield of 2,3-epoxypropanation (%) [(a)]	
	Free radical addition [(b)]	Thermolysis [(c)]	Free radical addition [(b)]	Thermolysis [(c)]
	70	30	67	33
	48	35	78	70
$\underset{c}{CH_3}\underset{a}{CH_2}CO_2\underset{b}{CH_3}$	66 [(d)] [(e)]	55 [(d)] [(e)]	62 [(e)] [(f)]	44 [(e)] [(f)]
 $CH_3CH_2\underset{O}{\underset{\|}{C}}CH_2CH_3$	52	37	[(g)]	[(g)]
CH_3CN	60	17	32	25
CH_2Cl_2	68	63	74	35

[(a)] Measured on the isolated material relative to the starting peroxidic compound 1 or 2 [(b)] Molar ratio ZH/1/benzoyl peroxide=50/1/0.1 at 80°C for 24 h ; Molar ratio ZH/2/tert-butyl peracetate=100/1/0.1 at 110°C for 12 h [(c)] Optimal yields of isolated compounds taken from[7] and [9] [(d)] Presence of the substituted derivatives on *a* and *b* : free radical addition *a*/*b*=96/4 ; thermolysis *a*/*b*=96/4 [(e)] The pure substituted compounds were easily isolated by liquid-solid chromatography on silica [(f)] Presence of the substituted derivatives on *a*,*b* and *c* : free radical addition *a*/*b*+*c*=93/7 ; thermolysis *a*/*b*+*c*=87/13 [(g)] The epoxy ketone was not stable in the reaction conditions leading to several compounds.

The difference in the efficiency of functionalization of tetrahydrofuran and acetonitrile through their free radical additions to the perester and the peroxide cannot be explained by the polar character of the two radicals. Indeed, either the nucleophilic cyclohexyl and tetrahydrofuryl-2 radicals or the electrophilic cyanomethyl and methoxycarbonyl-1 ethyl-1 radicals add differently to the unsaturated compounds 1 and 2. As we previously demonstrated[9b] allyl-tert-butyl peroxide decomposes more readily in acetonitrile than in cyclohexane, presumably through an unknown "ionic process". Conversely the perester appears to be stable enough in this solvent to give free radical adducts. This result is surprising considering that peresters are generally much more sensitive to the polarity of the solvent, being well-known compounds for ionic isomerization[10], and that, to our knowledge, such reactions have not been described for alkyl peroxides. A confirmation of this instability of 2 in acetonitrile was obtained by the study of the decomposition of benzoyl peroxide at 80°C in an acetonitrile solution of 2 with yields of epoxide approaching 50 %. The unknown process by which 2 was consumed, was sufficiently slowed to allow competition by the radical process.

FREE RADICAL ADDITIONS OF ZH TO SUBSTITUTED PEROXIDIC COMPOUNDS

As previously shown in reviews dealing with free radical additions to double bonds[1], the rate of addition is dependent on the degree of substitution of the ethylenic carbons. To define the limitations of the addition-elimination process for unsaturated peroxy compounds we applied the reaction to the following model peresters and peroxides :

$CH_2{=}C(CH_3)-(CH_2)_2-CO_3tBu$ 1a

$(CH_3)_2C{=}CH-(CH_2)_2-CO_3tBu$ 1b

$CH_2{=}C(CH_3)-CH_2-OOtBu$ 2a

$(CH_3)_2C{=}CH-CH_2-OOtBu$ 2b

As steric effects could also be involved in the homolytic displacement step, other models have been designed to complete the analysis of such parameters :

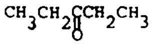
$CH_2{=}CH-CH_2-C(CH_3)_2-CO_3tBu$ 1c

$CH_2{=}CH-C(CH_3)_2-OOtBu$ 2c

Unfortunately, at the moment, no synthesis of 2c has been efficient.

Table 6 shows that free radical additions to 1a and 2a are operative. As predicted, the experiments conducted with 1b and 2b did not lead to the desired compounds. The main part of the peroxidic substrate was recovered, unreacted, for the three studied solvents (cyclohexane, dichloromethane, methyl propionate).

Table 6. Yields of lactones and epoxides from addition of ZH to 1a, 1c and 2a

ZH	Peroxidic compounds	Yield of lactone (%) 1a	Yield of lactone (%) 1c	Yield of epoxide (%) 2a
		44	28	49
		42	26	77
$CH_3CH_2CO_2CH_3$		60	24	52
 $CH_3CH_2\underset{O}{\underset{\|}{C}}CH_2CH_3$		35	19	(a)
CH_3CN		41	33	20
CH_2Cl_2		38	26	60

[a] See table 2 footnote g

From the comparison of the yields of lactones (reactions of ZH with 1, 1a, 1b, 1c) and epoxides (reactions of ZH with 2, 2a, 2b), preliminary conclusions can be given :

i) the reaction appears to obey the classical laws of free radical addition.

ii) the yield of functionalized ZH decreases with increasing substitution of the carbon attacking the O-O bond (compare 1 and 1a, 2 and 2a).

iii) for the lactone synthesis, the presence of α-carboxy substituents certainly causes a steric constraint which disfavours the homolytic displacement (compare 1 and 1c).

However, to draw more quantitative conclusions, these reactions have to be much more carefully studied, leading to an accurate balance of all the formed compounds. This analysis is beyond the scope of our intentions.

CONCLUSION

As the main result of this study, we want to underline the synthetic potential of the induced decomposition of unsaturated peroxy compounds. Indeed, free radical additions of hydrogen donor solvents (ZH) to tert-butyl peresters of pent-4-enoic, 4-methyl-pent-4-enoic and 2,2-dimethyl-pent-4-enoic acids lead to substituted γ-butyrolactones. Epoxides were obtained in a similar manner when this addition-elimination was applied to allyl or methallyl-tert-butyl peroxides. However these reactions were inoperative when the double bond was trisubstituted.

EXPERIMENTAL

Techniques

An Intersmat IGC 112 F (flame ionization ; N_2) was used for the gas chromatographic analyses, which were carried out on stainless steel columns (length 1.5 m, diameter 2 mm) of FFAP (10 % on Chromosorb WAW, 80/100 mesh), OV-17 (10 % on Chromosorb WHP, 80/100 mesh), OV-275 (10 % on Chromosorb WHP, 80/100 mesh).

^1H NMR spectra were recorded on a Perkin-Elmer R 12B spectrometer - CCl_4 solvent;ppm TMS=0 -; ^{13}C NMR spectra were measured on a Bruker WP60 spectrometer, fitted with a BNC 12 calculator - $CDCl_3$ solvent ; ppm TMS=0 - ; mass spectra were analyzed on Micromass 16F and 70-70 spectrometers (electronic ionization 70 eV).

General procedures

Experiments to define ZH/1 or 2/initiator molar ratios : a sealed ampule containing 2 ml of the three component solution was heated in an oil bath for the various duration and temperature combinations (see Tables). Yields of the expected functionalized solvents were obtained by gas chromatographic analyses of the reaction mixtures, using an internal standard.

Preparative scale experiments :

i) ZH boiling point $< \theta$ reaction : a steel bomb containing the solution of 1 or 2 and the initiator (1 : benzoyl peroxide ; 2 : tert-butyl peracetate) in the appropriate ZH solvent was heated in a thermostated oven (1 : 80°C, 24 h ; 2 : 110°C, 12 h).

ii) ZH boiling point $> \theta$ reaction : a round bottom flask, fitted with a condenser, containing the ZH solution of the unsaturated peroxidic compound and the initiator was set in an oil bath at the appropriate temperature for the expected time.

After the reaction, the solvent excess was removed by distillation. The lactones were separated by liquid-solid chromatography on silica gel column (35/70 mesh) ; the 2,3-epoxypropanated solvent was distillated at reduced pressure from the residual product.

For the *thermolyses*, 1 or 2 was considered as the initiator (1: 110°C, 12 h ; 2: 140°C, 10 h) and the same purification techniques were used.

Starting materials

Most of the reactants are commercially available and were purified before any use.

1-bromo-3-methyl-2-butene was prepared from isoprene as Ultee[17]. *Pent-4-enoic acid* and *3-methyl-pent-4-enoic acid* were obtained through the classical malonic synthesis ; allylation of methyl isobutyrate, using Rathke's method[18], followed by saponification, led to *2,2-dimethyl-pent-4-enoic acid*. Spectral and physical features of these acids were in good agreement with literature references[19,20,21].

Tert-butyl peresters were prepared quantitatively by the classical reaction of the acid chloride with tert-butyl hydroperoxide in pentane in presence of pyridine[10]. Purification over silica gel (35/70 mesh) was necessary to eliminate all acid traces.

Tert-butyl perpent-4-enoate $CH_2{=}CH(CH_2)_2CO_3C(CH_3)_3$

n_D^{20}= 1.4319 ; ^1H NMR : 6.2-4.9, m, 3H($CH_2{=}CH$) ; 2.6-2.2, m, 4H(CH_2-CH_2) ; 1.3, s, 9H $(CH_3)_3C$

Tert-butyl 4-methyl-perpent-4-enoate $CH_2{=}C(CH_3)(CH_2)_2CO_3C(CH_3)_3$

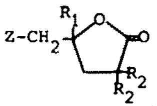
n_D^{20}= 1.4348 ; ^1H NMR : 4.8, m, 2H(CH_2=) ; 2.5-2.3, m, 4H(CH_2-CH_2) ; 1.8, s, 3H (CH_3) ; 1.3, s,9H $(CH_3)_3C$

Tert-butyl 2,2-dimethyl-perpent-4-enoate $CH_2{=}CHCH_2C(CH_3)_2CO_3C(CH_3)_3$

n_D^{20}= 1.4308 ; ^1H NMR : 6.2-4.8, m, 3H($CH_2{=}CH$) ; 2.3, d(J= 6 Hz), 2H(CH_2) ; 1.4, s, 9H$(CH_3)_3C$; 1.2, s, 6H$(CH_3)_2C$

Tert-butyl 5-methyl-perhex-4-enoate $(CH_3)_2C{=}CH$-$(CH_2)_2CO_3C(CH_3)_3$

n_D^{20}= 1.4379 ; ^1H NMR : 5.3-4.8, m, 1H(CH=) ; 2.5-2.2, m, 4H (CH_2-CH_2) ; 1.8 and 1.5, 2s, 6H $(CH_3)_2C$; 1.3, s, 9H $(CH_3)_3C$

Table 7 . Physical characteristics and spectral data[(a)] of the lactones 

Solvent ZH	R_1	R_2	b.p.(°C/Torr)	m.p. or n_D^{20}	^{1}H NMR
Cyclohexane	H	H	116-8(0.3)	35	4.8-4.2, m, 1H(CH-O) ; 2.7-0.9, m, 17H
Tetrahydrofuran	H	H	116-7(0.3)	1.4697	4.9-4.3, m, 1H(CH-O) ; 4.2-3.4, m, 3H(-CH_2-O-CH-) ; 2.7-0.8, m, 10 H
Methylpropionate	H	H	128-9(1)	1.4562	4.7-4.0, m, 1H(CH-O) ; 3.6, s, 3H(CH_3-O) ; 2.9-1.5, m, 7H ; 1.2, d (J= 8 Hz), 3H(CH_3-CH)
3-Pentanone	H	H	115-7(0.4)	1.4619	4.7-4.0, m, 1H(CH-O) ; 3-0.6, m, 15H
Dichloromethane	H	H	114-5(0.25)	1.4887	6.0-5.7, m, 1H($CHCl_2$) ; 4.8-4.3, m, 1H (CH-O) ; 2.7-1.7, m, 6H
Acetonitrile	H	H	125-8(0.8)	1.4518	4.8-4.3, m, 1H(CH-O) ; 2.8-1.5, m, 8H
Cyclohexane	CH_3	H	(b)	1.4819	2.7-0.7, m, 17H ; 1.4, s, 3H (R_1)
Tetrahydrofuran	CH_3	H	(b)	1.4704	4.1-3.4, m, 3H (-CH_2-O-CH-) ; 2.7-0.8, m, 10 H ; 1.4, s[(c)], 3H (R_1)
Methylpropionate	CH_3	H	(b)	1.4572	3.6, s, 3H(CH_3-O) ; 2.8-1.6, m, 7H ; 1.4, s[(c)], 3H(R_1) ; 1.1, d(J= 8 Hz), 3H(CH_3-CH)
3-Pentanone	CH_3	H	(b)	1.4629	2.9-0.9, m, 15H ; 1.4, s[(c)], 3H(R_1)
Dichloromethane	CH_3	H	(b)	1.4818	6.1-5.8, m, 1H($CHCl_2$) ; 2.7-1.6, m, 6H ; 1.4, s, 3H(R_1)
Acetonitrile	CH_3	H	(b)	1.4529	2.8-1.6, m, 8H ; 1.4, s, 3H(R_1)
Cyclohexane	H	CH_3	(b)	1.4905	4.7-4.2, m, 1H(CH-O) ; 2.6-0.8, m, 15H ; 1.3, s, 6H(R_2)
Tetrahydrofuran	H	CH_3	(b)	1.4708	4.9-4.3, m, 1H (CH-O) ; 4.2-3.7, m, 3H (-CH_2-O-CH-) ; 2.7-1.6, m, 8H ; 1.4, s, 6H (R_2)
Methylpropionate	H	CH_3	(b)	1.4582	4.7-4.1, m, 1H(CH-O) ; 3.6, s, 3H(CH_3-O) ; 2.8-1.6, m, 5H ; 1.4, s, 6H(R_2) ; 1.2, d(J=8 Hz), 3H(CH_3-CH)
3-Pentanone	H	CH_3	(b)	1.4641	4.7-4.1, m, 1H(CH-O) ; 3.0-1.0, m, 13H ; 1.4, s, 6H (R_2)
Dichloromethane	H	CH_3	(b)	1.4767	6.1-5.7, m, 1H($CHCl_2$) ; 4.7-4.2,m, 1H(CH-O) ; 2.9-1.6, m, 4H ; 1.3, s, 6H (R_2)
Acetonitrile	H	CH_3	(b)	1.4567	4.8-4.3, m, 1H(CH-O) ; 2.8-1.6, m, 6H ; 1.3, s, 6H (R_2)

(a) Mass spectra : when R_1=R_2=H an important peak, often the base peak, was observed at m/z = 85 ; when R_1=CH_3 and R_2=H the same phenomena occurred at m/z = 99 and when R_1=H,R_2=CH_3 two characteristic peaks were observed at m/z = 69 and 41. (b) Isolated by silicagel chromatography . (c) The singulet is doubled showing the presence of both diastereoisomers.

Table 8 . Physical characteristics and spectral data of the epoxides

Solvent ZH	R_1	R_2	b.p. (°C/Torr)	n_D^{20}	^{1}H NMR
Cyclohexane	H	H	85-7(25) Lit.[23] 55-56(2)	1.4609 Lit.[24] 1.4575	3.1-2.1, m, 3H(CH_2-O-CH) ; 2.1-0.4, m, 13H(C_6H_{11}-CH_2)
Tetrahydrofuran	H	H	92-3(25)	1.4510	4.0-3.3, m, 3H(CH_2-CH_2-O-CH-CH_2) ; 3.1-2.3, m, 3H(CH_2-O-CH) ; 2.2-1.0, m, 6H
Methylpropionate	H	H	96-101(25)	1.4330	3.6, s, 3H(CH_3-O) ; 3.1-2.3, m, 4H(CH_2-O-CH, CH-CO_2) ; 2.0-1.4, m, 2H(CH_2-CH-O) ; 1.2, d (J= 7 Hz), 3H(CH_3-CH)
Dichloromethane	H	H	70(25)	1.4680	6.1-5.7, m, 1H($CHCl_2$) ; 3.3-2.1, m, 5H(CH_2-O-CH-CH_2)
Acetonitrile	H	H	106-110(25) Lit.[24] 47-49(0.25-0.4)	1.4356	(C_6D_6) 2.7-1.7, m, 5H(CH_2-O-CH , CH_2CN) ; 1.5-1.1, m, 2H(CH_2-O-CH-CH_2)
Cyclohexane	CH_3	H	95(25)	1.4568	2.4, s, 2H(CH_2-O) ; 1.1, s, 3H(R_1) ; 2.1-0.5, m, 13H(C_6H_{11}-CH_2)
Tetrahdrofuran	CH_3	H	93(25)	1.4478	4.2-3.3, m, 3H(CH_2-CH_2-O-CH-CH_2) ; 2.8-1.5, m, 8H(CH_2-CH_2 , CH_2-O-C-CH_2) ; 1.3, s, 3H(R_1)
Methylpropionate	CH_3	H	100(25)	1.4296	3.6, s, 3H(CH_3-O) ; 2.8-1.4, m, 5H(CH_3-CH-CO_2 , CH_2-O-C-CH_2) ; 1,2, s, 3H(R_1) ; 1.1, d(J= 7 Hz), (CH_3-CH)
Dichloromethane	CH_3	H	75(25)	1.4657	5.9-5.6, m, 1H($CHCl_2$) ; 2.9-2.0, m, 4H(CH_2-O-C-CH_2) ; 1.4, s, 3H(R_1)
Acetonitrile	CH_3	H	110(25)	1.4303	(C_6D_6) 1.6, s, 2H(CH_2-O) ; 1.4-0.5, m, 4H(CH_2-CH_2-CN) ; 0.4, s, 3H(R_1)

Tert-butyl peracetate was prepared as[22].

The synthesis of the *diperester* derived from 2-N-methylaminoethanol was performed as previously described[12].

Allylic tert-butyl peroxides were obtained from allylic halides and tert-butyl hydroperoxide, using a phase transfer procedure[9]. Distillation under vacuum of the rough product gave the pure peroxide.

Allyl-tert-butyl peroxide $CH_2=CHCH_2OOC(CH_3)_3$

n_D^{20}= 1.4051 ; Eb_{45} = 42°C ; ^1H NMR : 6.3-4.9, m, 3H($CH_2=CH$) ; 4.3, d (J= 8 Hz), 2H(CH_2O) ; 1.2, s, 9H$(CH_3)_3C$ (Lit.[13])

2-methallyl-tert-butyl peroxide $CH_2=C(CH_3)CH_2OOC(CH_3)_3$

n_D^{20}= 1.4099 ; Eb_{25} = 46°C ; ^1H NMR : 4.9, m, 2H(CH_2=) ; 4.3, m, 2H(CH_2O) ; 1.7, s, 3H(CH_3) ; 1.2, s, 9H$(CH_3)_3C$

3-methyl-but-2-enyl-tert-butyl peroxide $(CH_3)_2C=CHCH_2OOC(CH_3)_3$

n_D^{20}= 1.4283 ; Eb_{25} = 70°C ; ^1H NMR : 5.3, t (J= 8 Hz), 1H(CH=) ; 4.3, d (J= 8 Hz), 2H(CH_2O) ;1.8 and 1.7 , 2s$(CH_3)_2C$; 1.2, s, 9H$(CH_3)_3C$

Reaction products

The physical and spectral features of the different functionalized solvents are summarized in tables 7 and 8.

AKNOWLEDGEMENT

We thank Professor R. LALANDE (University of Bordeaux I) for his interest in this work.

REFERENCES

(1) Walling, C. ; Huyser, E.S. In "Organic Reactions" ; Wiley and Sons : New-York, 1963 ; Chapter 3 and references therein.
Stacey, F.W. ; Harris, J.F. *Ibid.* Chapter 4 and references therein.
Sosnovsky, G. "Free Radical Reactions in Preparative Organic Chemistry" ; Mac Millan Company : New-York, 1964 ; Chapters 1-6 and references therein.
Huyser, E.S. "Free Radical Chain Reactions" ; Wiley and Sons : New-York, 1970 ; Chapters 6-7.
Abell, P.I. In "Free Radicals" ; Kochi, J.K., Ed.; Wiley Interscience : New-York, 1973 ; Vol.2, Chapter 13.

(2) Cazaux, M. ; Lalande, R. *Bull. Soc. Chim. Fr.* 1966, 3381.
Paskoff, B. ; Cazaux, M. ; Lalande, R. *Bull. Soc. Chim. Fr.* 1968, 2946.
Paskoff, B. ; Cazaux, M. ; Lalande, R. *Bull. Soc. Chim. Fr.* 1970, 624.
Cazaux, M. ; Lalande, R. *Bull. Soc. Chim. Fr.* 1971, 461.
Cazaux, M. ; Maillard, B.; Lalande, R. *Comptes rendus (C)* 1972, 1133.
Cazaux, M. ; Lalande, R. *Bull. Soc. Chim. Fr.* 1972, 1887.
Maillard, B. ; Cazaux, M. ; Lalande, R. *Bull. Soc. Chim. Fr.* 1973, 1368.

(3) Jaouhari, R. ; Filliatre, C.; Maillard B.; Villenave J-J. *Tetrahedron* 1982, *38*, 3137.

(4) Jaouhari, R. ; Maillard , B. ; Filliatre, C. ; Villenave J-J. *Synthesis* 1982, 760.

(5) Tidwell, T.T. In "Organic Free Radicals" ; Pryor, W.A., Ed.; *ACS Symp. Ser.* 1978 ; Vol.69, pp. 102-121.

(6) Ingold, K.U. ; Roberts, B.P. "Free Radical Substitution Reactions" ; Wiley Interscience : New-York, 1971 ; Chapter 7 and references therein.
Bloodworth, A.J. ; Davies, A.G.; Griffin, I.M. ; Muggleton, B. ; Roberts, B.P. *J. Am. Chem. Soc.* 1974, *96*, 7599.
Porter, N.A. ; Nixon, J.R. *J. Am. Chem. Soc.* 1978, *100*, 7116.
Porter, N.A. ; Cudd, M.A. ; Miller, R.W. ; Mc Phail, A.T. *J. Am. Chem. Soc.*, 1980, *102*, 414.
Bloodworth, A.J. ; Courtneidge, J.L. *J. Chem. Soc., Chem. Commun.* 1981, 1117 and previous papers.
Sway, M.I. ; Waddington, D.J. *J. Chem. Soc., Perkin Trans. 2* 1983, 139 and previous papers.
Corey, E.J. ; Schmidt, G. ; Shimoji, K. *Tetrahedron Lett.* 1983, *24*, 3169.

(7)a Maillard, B. ; Kharrat, A. ; Gardrat, C. *Tetrahedron* 1984, *40*, 3531.
b Kharrat, A. ; Maillard, B. ; Gardrat, C. *Synth. Commun.* 1983, *13*, 1209.
c Kharrat, A. ; Gardrat, C. ; Maillard, B. *Can. J. Chem.* 1984, *62*, 2385.
d Kharrat, A. ; Gardrat, C. ; Maillard, B. *Can. J. Chem.*, submitted for publication.
e Kharrat, A. ; Gardrat, C. ; Maillard, B. *Bull. Soc. Chim. Belg.*, in press.

(8) Maillard, B. ; Kharrat, A. ; Gardrat, C. , to be published.

(9)a Maillard, B. ; Montaudon, E. ; Rakotomanana, F.; Bourgeois, M.J. *Tetrahedron*, in press.
b Rakotomanana, F. ; Montaudon, E. ; Maillard, B. *Tetrahedron*, submitted for publication.
c Rakotomanana, F. ; Montaudon, E. ; Maillard, B., to be published.

(10) Singer, L.A. In "Organic Peroxides" ; Swern, D., Ed. ; Wiley Interscience : New-York, 1970 ; Vol. 1, Chapter 5.

(11) Bop, J.P. ; Filliatre, C. ; Maillard, B. ; Villenave, J-J. *Thermochimica Acta* 1981, *43*, 339.

(12) Bourgeois, M.J. ; Maillard, B. *Eur. Polym. J.* 1983, *19*, 419.

(13) Hiatt, R. ; Nair, V.G.K. *Can. J. Chem.* 1980, *58*, 450.

(14) Hiatt, R. In "Organic Peroxides" ; Swern, D., Ed. ; Wiley Interscience : New-York, 1970 ; Vol. 2, Chapter 8.

(15) Filliatre, C. ; Maillard, B. ; Villenave, J-J. *Thermochimica Acta* 1980, *39*, 195.

(16) Kaptein, R. In "Advances in Free Radical Chemistry" ; Williams, G.H., Ed. ; Elek Science : London, 1975 ; Vol. 5, Chapter 5.

(17) Ultee, A.J. *Recl. Trav. Chim. Pays-Bas* 1949, *68*, 125.

(18) Rathke, M.W. ; Lindert A. *J. Am. Chem. Soc.* 1971, *93*, 2318.

(19) Linstead, R.P. ; Rydon, R.M. *J. Chem. Soc.* 1933, 583.

(20) Bowman, R.E. ; Mason, R.G. *J. Chem. Soc.* 1952, 4151.

(21) Brown, R.F. ; Van Gulick, N.M. *J. Am. Chem. Soc.* 1955, *77*, 1092.

(22) Bartlett, P.D. ; Hiatt, R.R. *J. Am. Chem. Soc.* 1958, *80*, 1398.

(23) Chirko, A.I. ; Tischenko, I.G. ; Golovataya, V.S. *Vesti Akad. Nauk. Beloruss. SSR, Ser. Khim. Nauk* 1973, *6*, 74.

(24) Hall, H.K. ; Blanchard, E.P. ; Cherkofsky, S.C. ; Sieja, J.B. ; Sheppard, W.A. *J. Am. Chem. Soc.* 1971, *93*, 110.