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Stereoselectivity of the Intramolecular Homolytic Substitution in the Induced Decomposition of Methacrylic-type Peroxidic Compounds

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Abstract: The stereochemistry of the oxiranes, obtained by radical induced decomposition of various peroxydic compounds, was determined by NMR spectroscopy. The stereoselectivity of the intramolecular homolytic substitution on the peroxidic bond was discussed in relation to the effect of the reaction temperature and on the influence of structural factors such as the nature of the leaving and attacking radicals. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Over the past decade, numerous works have shown that radicals have an enormous potential for applications in stereoselective reactions[1]. In order to develop the synthetic potential of the induced decomposition of peroxidic compounds bearing an "acrylic" unsaturation, a wide variety of glycidic esters were prepared and reported through the homolytically induced decomposition of methacrylic-type peroxidic compounds (*e.g.* addition of a carbon-centered radical on the unsaturation and subsequent S_Hi reaction on the O-O bond). Scheme 1 summarizes the peroxy derivatives studied and the oxiranes obtained in the present work. Carbon-centered radicals R• can be generated from oxyl radicals ZO• by various ways: (1) hydrogen atom abstraction to a solvent RH[2,3]; (2) rearrangements (*e.g.* β-scission, cyclisation, 1,5-H translocation) of oxyl radicals to alkyl ones, which add directly to peroxy derivatives (2a)[4,5] or efficiently transfer an iodine atom on an iodo derivative RI to yield other kinds of alkyl radicals (2b)[6]; (3) abstraction of an iodine atom

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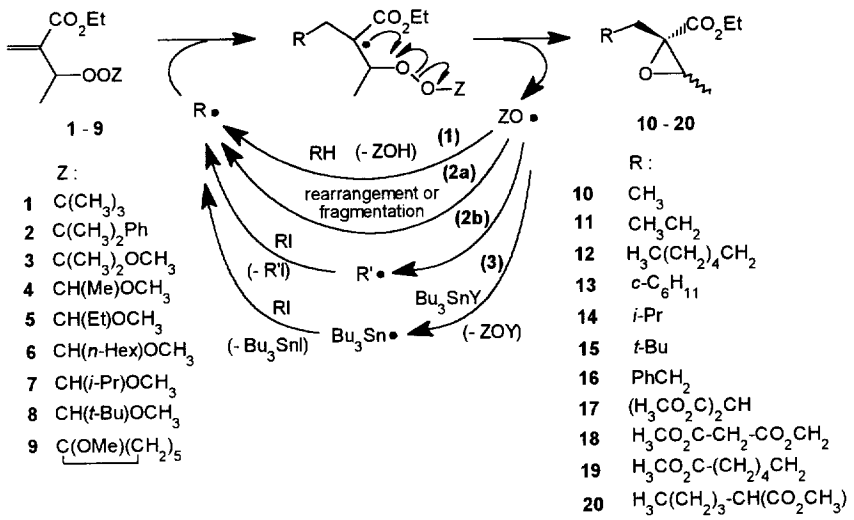
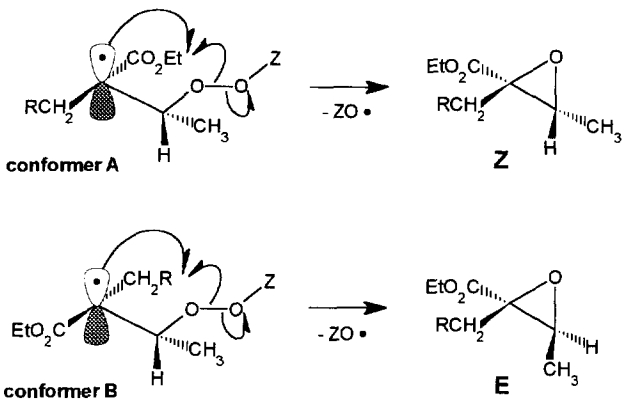
from an iodocompound RI, involving $Bu_3Sn\bullet$ as relay radicals[7]. These methacrylic-type peroxycompounds were also used as efficient chain transfer agents in radical polymerization to afford α,β-difunctional oligomers[8].



Scheme 1. General Mechanism for the radical decomposition of peroxy derivatives **1-9**.

The formation of two diastereoisomers in the induced decomposition of some unsaturated peroxides and the preferential formation of an *E*-isomer can be explained by the occurence of two possible reaction pathways (Scheme 2). Indeed, Porter *et al.*[9] demonstrated that the transition state of S_Hi yielding three-membered rings exhibits an alignment of the attacking radical and both oxygens of the peroxidic bond. Thus, it is clear that, for steric reasons, two conformers A and B are possible for the adduct radical to afford two isomeric heterocycles. The possibility of the formation of heterocyclic *Z*- and *E*-diastereoisomers is mainly due to the presence of a methyl fragment on the chain linking both reacting functional groups. Indeed, these schemes show a steric hindrance between CH_3 and CO_2Et on one hand and between RCH_2 and CH_3 on the other, in the conformers A and B, respectively.

In the present paper, the stereoselectivity of the S_Hi reaction on peroxidic compounds **1-9** has been investigated. The influence of the steric hindrance of the leaving groups OZ and those of the radical which add onto the peroxide, as well as the effect of the reaction temperature in the case of peroxyketal **9**, has been studied. The influence of the steric hindrance of the ester fragment or of the group located in the allylic position of the peroxides (a methyl fragment in the present case) has not been investigated. Two different initiating systems, based on the thermal homolysis of *tert*-butyl peracetate (TBPA) or α,α′-azobis(isobutyronitrile) (AIBN) and on the autoxidation of triethylborane, were used in this work.



Scheme 2. Stereoselectivity in the intramolecular homolytic substitution on O-O bond.

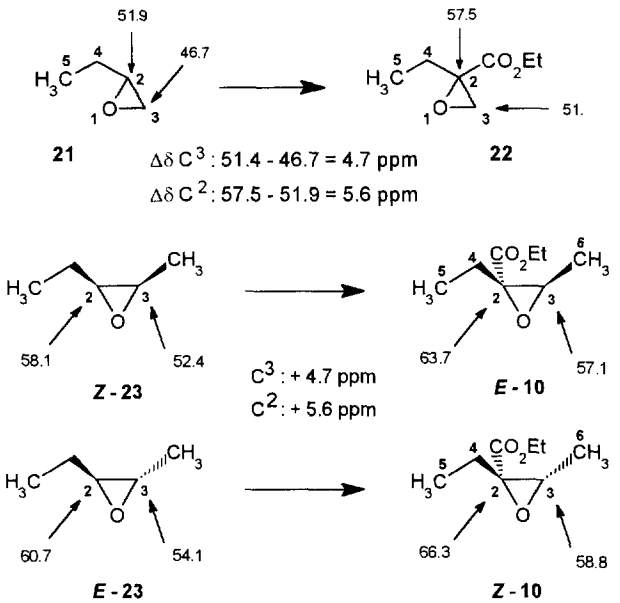
RESULTS AND DISCUSSION

Influence of the leaving fragment

We reported recently that peroxidic compounds **1-3** are inductively decomposed in benzene under radical conditions (110°C, 12 h, TBPA as initiator) to afford oxiranes **10** in 67, 83 and 92% yield respectively, as a mixture of two diastereoisomers. The ratio of the two isomers, relatively constant whatever the precursor used, was determined by GC to be close to 13 / 87, based on a similar chromatographic factor for isomers *Z* and *E*. The proportion of each isomer is not influenced by the stereochemistry of the reaction, as it was already reported by Lubeigt *et al.*[10] in the case of the synthesis of disubstituted oxiranes, in contrast to the case of the synthesis of tetrahydrofuran derivatives[11]. It has also been confirmed that the values obtained for the molar ratios of isomers (*Z* / *E*) did not result from a thermodynamic equilibrium of the reaction. No isomerization of the diastereoisomeric heterocycles occured throughout the reaction period: samples were taken every 20 min from the reaction medium and showed that the ratios *Z* / *E* stay constant. These results are in accordance with the hypothesis that the reaction is under kinetic control.

The stereochemical attribution of the two heterocyclic diastereoisomers was based on the analysis of the ^{1}H and ^{13}C NMR spectra of the corresponding mixtures. Signals for each isomer were identified (which is not difficult when they are present in different amounts) and the structure of *Z*- and *E*-isomers was determined by analogy of the chemical-shift differences of various carbons and protons of the heterocycles with those of similar model molecules, described in the literature. The attribution *Z* / *E* is realized by comparison of the chemical shift variations ($\Delta\delta$) for carbons of both isomers, with the values of the corresponding model compounds reported in the literature, when known (Scheme 3). To determine the chemical shifts of carbons C^2 and C^3 for isomers *Z* and *E* of **10**, an empirical estimation was used. The comparison of chemical shifts of carbons C^2 and C^3 of 1,2-epoxybutane **21** and of **22** (prepared by Navarro *et al.*[12]) afford the values of the

difference of chemical shifts for each carbon, due to its structural modifications (Table 2). Thus, it is possible to estimate the chemical shifts of carbons C^2 and C^3 of diastereoisomers *Z* and *E* of **10** from the known values of the chemical shifts of isomers *Z* and *E* of 2,3-epoxypentane **23** [13] and from $\Delta\delta\ C^2$ and $\Delta\delta\ C^3$, respectively.



Scheme 3. Z/E attribution for diastereoisomers **10** by empirical analysis.

In Table 1 are mentioned experimental and calculated chemical shifts for carbon C^3 and C^2 of both isomers of **10**. Taking into account the low chemical shift difference for C^3 and the incertitude of such a method, correlation of experimental and theoretical values have been done only in the case of carbon C^2, based on a comparison of the relative rather than the absolute values of chemical shifts. The formation of the *E*-isomer is based on the preferential conformation B (Scheme 2), in which bulkier vicinal substituents are removed from each other.

Table 1. ^{13}C NMR Chemical Shifts[a] of Asymmetric Carbons and Attribution *Z* / *E* for Diastereoisomers of **10**.

attribution	C^3		C^2	
E	calcd.	exp.	calcd.	exp.
(major)	*57.1*	58.2	*63.7*	61.6
Z	calcd.	exp.	calcd.	exp.
(minor)	*58.8*	58.2	*66.3*	63.9

[a] δ in ppm (from TMS : δ = 0 ppm).

^{13}C NMR chemical shifts of 1,1-Dichloro-3,4-epoxypentane **24** and 2,3-epoxypentane **23** [13] are reported in Table 2 and compared to **10** and ethyl 2,3-epoxy-2-ethylpropenoate **23**. Identification of chemical shifts for carbons C^4, C^5, and C^6 was much more easier than those of carbons C^2 and C^3. Indeed, it is known that, in the case of oxiranes bearing two vicinal substituents (C^6H_3 and $C^4H_2CH_3$ (**10**), or $C^4H_2CHCl_2$ (**24**)), carbon C^4 and C^6 are shifted to higher chemical shifts by γ effect in the *E*-isomer than for the *Z*-isomer.

Table 2. ^{13}C NMR Chemical Shifts[a] of Various 1,2-Substituted Oxiranes.

oxirane		C^2	C^3	C^4	C^5	C^6	ref.
22		57.5	51.4	24.1	8.7	/	12
23	*E*	60.7	54.1				13
	Z	58.1	52.4				
24	*E*	56.0 [b]	55.3 [b]	46.6	70.9	17.8	10
	Z	52.9 [b]	53.6 [b]	42.4	71.2	13.9	
10	*E*	61.7	58.4	20.8	9.4	14.1	this
	Z	64.1	58.3	26.2	8.7	14.3	work

[a] δ in ppm (from TMS : δ = 0 ppm). [b] determined from theoretical chemical shift obtained by the method of incrementation.

Influence of the radical adding to the unsaturation

The stereoselectivity of the S_Hi in the induced decomposition of **1** by various radicals R• has been investigated respectively in hydrogenated solvents (cyclohexane, dimethyl malonate) (Table 3)[2]. However, hydrogen abstraction of the solvent to produce radicals is not selective enough to afford efficiently one kind of radical when several hydrogen types are present on the solvent[3], as it is in the case of dimethyl malonate.

Table 3. Effect of the Nature of the Radical R• on the Stereochemistry of the Induced Decomposition of **1** in Cyclohexane and Dimethyl Malonate at 110°C [a]. Determination of the Molar Ratios *Z* / *E* by GC for the Corresponding Oxiranes and ^1H NMR Chemical Shifts of the "Epoxidic" Hydrogen C^3-H.

oxirane	yields [b] (%)	δ *Z*-C^3H [c]	δ *E*-C^3H [c]	*Z* / *E* [d]
10	5 [e], 57 [f]	3.01	3.21	13 / 87
13	84 [e]	2.92	3.08	14 / 86
17	14 [f]	3.05	3.20	13 / 87
18	16 [f]	3.04	3.18	13 / 87

[a] molar ratio solvent / **1** / TBPA = 20 / 1 / 0.1. [b] yield determined by GC and calculated from **1**. [c] ^1H NMR chemical shifts of C^3-H, determined in $CDCl_3$ from tetramethylsilane. [d] molar ratio determined by GC. [e] in cyclohexane. [f] in dimethyl malonate.

The size of the radical R• was shown to have no effect on the relative ratios of both isomeric heterocycles produced from the peroxide **1**. In a previous study, the synthesis of glycidic esters from **4-8** indicates a decrease in the yield of isolated epoxide with increasing bulkiness of the alkyl fragment of the aldehydic precursor of the peroxide. The present result on the GC analysis of the low-boiling product formed by decomposition of peroxyketals **4-8** confirmed the occurence of a concerted side-reaction of dihydrogen elimination (Table 4). Indeed, in the case of **3**, only the formation of the product formed after β-scission is observed (methyl acetate, 97%) whereas for **4-8**, one can identified only low amounts of the corresponding products (in the case of **8**, for example, only 15% of methyl formate). However, in that latter case, a significant amount of methyl 2,2-dimethylpropanoate (80%) is observed. Such a product can not be formed by the spontaneous homolytic decomposition of the corresponding peroxyketal because only a small amount of methanol (2%) and no ethyl 2-(1-hydroxyethyl)propenoate (the experimental confirmation of the low polymerizability of the latter compound was performed under the reaction conditions used[14]), which would be also formed in the thermolysis of **8**, were observed. Similar results were also reported recently by Helgorsky *et al.*[15] in the case of saturated peroxyketals.

Table 4. Yields [a] of esters (methyl alkanoates and formates) and oxiranes obtained from the induced decomposition of peroxyketals **4-8** in benzene, at 110°C [b].

R	CH_3	Et	n-C_6H_{11}	i-Pr	t-Bu
RCO_2CH_3 (%)	14	20	24	35	80
HCO_2CH_3 (%)	84	76	72	62	15
oxirane (%)	(**10**) 78	(**11**) 72	(**12**) 70	(**14**) 55	(**15**) 6
Z / E [c]	13 / 87	13 / 87	13 / 87	14 / 86	15 / 85

[a] yield determined by GC and calculated from the starting peroxyketal. [b] molar ratio benzene / peroxyketal **4-8** / TBPA = 20 / 1 / 0.1. [c] molar ratio determined by GC.

In order to produce radicals with precise structure, the use of halogenated compounds RI was investigated (Table 5). Alkyl radicals R•, produced by the fragmentation of the 1-methoxy-1-methylethoxyl radical formed in the induced decomposition of the peroxyketal **3**, yield the expected radical R• by atom transfer on alkyl iodide. Radical R• yields oxiranes **10-15** by further reaction with the double bond of the peroxydic compound. Ramon *et al.*[6] reported recently a quantitative preparation of oxiranes through a similar procedure in the presence of halogenated derivatives. It was expected that the rate of atom transfer from iodocompounds to methyl radicals is high enough[16] to compete with the addition of methyl radicals to **3**. Unfortuntely, even in the case of higher concentration of iododerivatives, it has not been possible to disfavour totally the addition side-reaction of methyl radicals. When the molar ratio RX / **3** = 3, peroxyketals **10** and **11** were obtained in 40 and 45 % yield, respectively. Anyway, molar ratios **10** / oxirane obtained from the various RX are in good agreement with the bond dissociation energies of these latter compounds. Similar to the results obtained for

the leaving group, the distance between the methyl fragment and the group R in the two conformers A and B of the adduct radical as well as in the heterocycle itself, exhibit nearly no effect in the molar ratio *Z* / *E* of the diastereoisomers. The bulkiness of the R fragment show a very low effect on the relative ratio of *Z* / *E* isomers only for the *t*-butyl group.

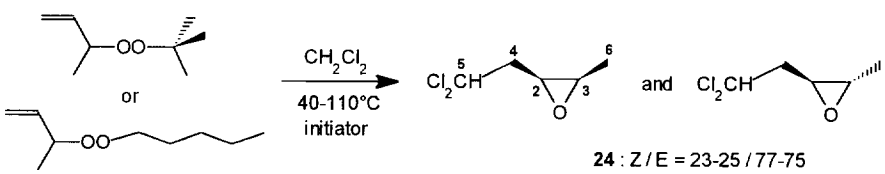
Table 5. Yields [a] and molar ratios *Z* / *E* [b] for oxiranes obtained from induced decomposition of **3** in benzene, at 110°C in the presence of halogenated compounds [c].

	EtI	*n*-$C_6H_{11}I$	*c*-$C_6H_{11}I$	*i*-PrI	$PhCH_2Br$	C_6H_5I
10 (%) [a]	59	55	40	31	70	88
oxirane (%)[a]	(**11**) 30	(**12**) 34	(**13**) 47	(**14**) 60	(**16**) 2	/
Z / *E* [b]	13 / 87	13 / 87	13 / 87	14 / 86	15 / 85	/
BDE [d]	242	242	228	228	257	320

[a] yield determined by GC and calculated from **3**. [b] molar ratio determined by GC. [c] molar ratio benzene / **3** / RX / TBPA = 20 / 1 / 1 / 0.1. [d] bond dissociation energies of R-X (in kJ/mol), estimated from ref. [17].

Influence of the temperature

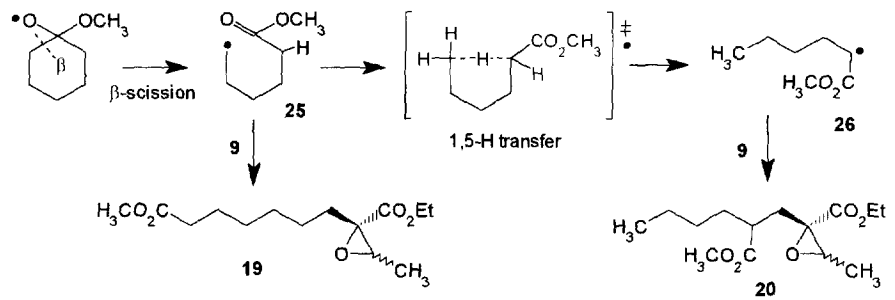
Lubeigt *et al.*[10] reported that the molar ratio *Z* / *E* of oxirane **24** was not affected by the variation of the reaction temperature (from 40 to 110°C), in the induced decomposition of either *t*-butyl or pentyl 1-methylpropenyl peroxide in dichloromethane (Scheme 4).



Scheme 4. Influence of the temperature on the induced decomposition of *t*-butyl 1-methylpropenyl peroxide and pentyl 1-methylpropenyl peroxide in dichloromethane.

The induced decomposition of peroxyketal **9** has been realized in benzene, at various temperatures (from 0 to 110°C), to determine the influence of the temperature on the stereoselectivity of the intramolecular homolytic substitution (Table 6). In order to carry out all experiments with the same initiator at the various temperatures investigated, the system BEt_3 / O_2 has been used in comparison with other initiating systems (AIBN, TBPA). As shown in Scheme 5, the 6-methoxycarbonylhexyl radical **25**, provided from the fragmentation of 1-methoxy-1-cyclohexyloxyl radical **26**, can evolve in two different processes, yielding oxiranes **19** or **20**. The stereoselectivity of the S_Hi reaction has been studied in the case of the major isomer **19**, formed by a mixture of two diastereoisomers only. The results shown in Table 6 indicate that the decrease

of the reaction temperature favored the formation of **19** and the relative proportion of the *E*-isomer. The isomerization of **25** by 1,5-hydrogen transfer, yielding **26**, involves a conformation of the transition state in which the atom radical C^1, the hydrogen atom, and carbon C^5 have to be colinear[18] (Scheme 5).



Scheme 5. Formation of epoxides **19** and **20** in the induced decomposition of peroxyketal **9** in benzene.

The molar ratio addition / 1,5-H transfer (AD / TR), indicating the increase of the regioselectivity of the reaction with the temperature, is in agreement with the hypothesis of the colinear transition state, because the thermal energy can favor the conformation yielding the intramolecular hydrogen transfer and the isomerization of the radical **25**. The similar molar ratio *Z* / *E*, obtained with BEt_3 and AIBN (80°C), or BEt_3 and TBPA (110°C), under different reaction times (1 to 12 hours), confirmed the kinetic control of the formation of the isomers.

Table 6. Effect of the temperature on the stereoselectivity of the induced decomposition of peroxyketal **9** in benzene[a].

Temp. (°C)	0	20	50	80	80	110	110
Initiator	BEt_3	BEt_3	BEt_3	BEt_3	AIBN	BEt_3	TBPA
19 (%) [b]	97	96	94	92	92	83	76
Z / *E* [c]	4 / 96	6 / 94	8 / 92	10 / 90	10 / 90	13 / 87	13 / 87
20 (%) [b]	3	4	6	8	8	14	13
AD / TR [d]	32	24	16	11.5	11.5	6	6

[a] molar ratio benzene / **9** / initiator = 20 / 1 / 0.1. [b] yield determined by GC and calculated from **9**. [c] molar ratio determined by GC (estimation by ^1H NMR for reaction performed at 110°C afford 15 / 85). [d] ratio addition / 1,5-H transfer (~ molar ratio **19** / **20**) for radical **25**.

EXPERIMENTAL

General Details. ^1H and ^{13}C NMR data were recorded on Bruker AC 250 spectrometer and obtained at 250 and 62.9 MHz, respectively. The solvent was $CDCl_3$ (δ_C = 77 ppm) and chemical shifts are reported relative to tetramethylsilane. Gas chromatographic (GC) analyses were performed with a silica capillary

column DB 5 (25 m by 0.1 mm). Cyclohexane and benzene were dried over sodium and dimethyl malonate was distilled before use. α,α'-Azobis(isobutyronitrile) was obtained from Fluka and recrystallized from methanol. 1 M solution of triethylborane in hexane, iodoethane, 1-iodohexane, 2-iodopropane, cyclohexyl iodide, benzyl bromide and phenyl iodide were purchased from Aldrich, and used without further purification. *t*-Butyl peracetate (TBPA) was prepared from *t*-butyl hydroperoxide and acetyl chloride, under basic conditions[19]. The initiating system BEt_3 / O_2 was reported by Brown *et al.*[20]. Peroxides **1** and **2** were synthesized according to Navarro *et al.*[21]. Peroxyketals **3-9** were prepared from ethyl 2-(1-hydroperoxyethyl) propenoate (obtained by the method reported by Adam and Griesbeck [22]) and the corresponding enol ethers or dimethyl acetals, respectively, according to the procedure described by Colombani and Maillard [5]. Oxiranes **10-20** were prepared and reported in previous papers[3,5].

TBPA and AIBN initiators. a mixture of a peroxydic compound (2 mmol) and an initiator (0.2 mmol, TBPA: 26 mg, AIBN: 33 mg) was added to a glass tube containing the amount of solvent (20 mmol, benzene: 1.56 g, cyclohexane: 1.68 g, dimethyl maloante: 2.64 g) required to produce a molar ratio solvent / peroxyderivative / initiator equal to 20 / 1 / 0.1. The glass tube was then sealed under reduced pressure (10^{-3} Torr) and heated 12 h (TBPA: 110°C, AIBN: 80°C). Yields of the expected compounds were obtained by GC analysis of the reaction mixture, using an internal standard. Molar ratios *Z* / *E* were estimated from the area of the corresponding signals, based on a similar chromatographic factor for *Z*- and *E*-isomers.

Et_3B / O_2 initiating system. 0.1 M solution of triethylborane in hexane (1 mL) was added dropwise over 30 min in a vigorously stirred solution of peroxyketal **9** (1 mmol) in benzene (1 mL), at various temperature. Continuous air bubbling was maintained in the reaction medium during the whole procedure. The reaction was monitored by GC by following the disappearance of the peroxyketal. If peroxyketal remained after an additional period of 30 min, a new portion of initiator (1 mL of Et_3B / hexane solution) was added in the medium until the complete disappearance of the peroxy derivative.

CONCLUSION

The induced decomposition of methacrylic-type peroxidic compounds exhibits some stereochemical features. The *E*-isomer was always the predominant product, irrespective of the starting compound involved, and its proportion increases with decreasing temperature. The size of the radical R• added to the unsaturation, and the size or the nature of the peroxydic group (OOZ) are inactive factors.

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