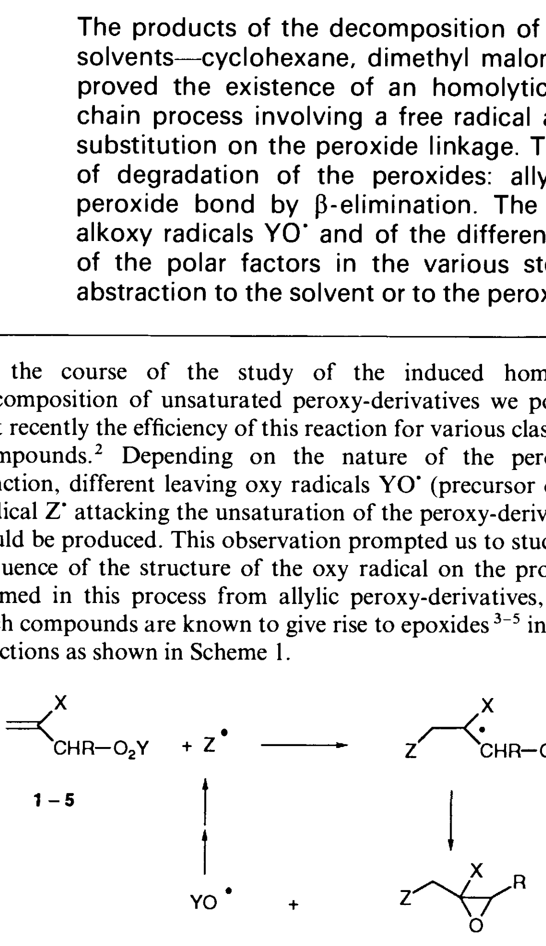
Intramolecular Homolytic Displacements. Part 22.[1] Polar Effects in the Homolytic Induced Decompositions of Allyl Peroxides

Daniel Colombani and Bernard Maillard *
Laboratoire de Chimie Organique et Organométallique, Associé au CNRS, URA 35, Université Bordeaux 1, 351, Cours de la Libération, F-33405 Talence Cedex, France

The products of the decomposition of allyl peroxides **1–5**, initiated by *tert*-butyl peracetate, in three solvents—cyclohexane, dimethyl malonate and benzene—were analysed. The formation of epoxides proved the existence of an homolytic induced decomposition of the unsaturated peroxides by a chain process involving a free radical addition to the double bond and an intramolecular homolytic substitution on the peroxide linkage. The balance of the reaction's products indicated a second way of degradation of the peroxides: allylic hydrogen abstraction followed by the breaking of the peroxide bond by β-elimination. The relative ratios of the products generated by the eliminated alkoxy radicals YO$^\cdot$ and of the different epoxides produced in these reactions showed the influence of the polar factors in the various steps of the homolytic induced decomposition: *i.e.* hydrogen abstraction to the solvent or to the peroxide and addition to the double bond.

In the course of the study of the induced homolytic decomposition of unsaturated peroxy-derivatives we pointed out recently the efficiency of this reaction for various classes of compounds.[2] Depending on the nature of the peroxidic function, different leaving oxy radicals YO$^\cdot$ (precursor of the radical Z$^\cdot$ attacking the unsaturation of the peroxy-derivative) could be produced. This observation prompted us to study the influence of the structure of the oxy radical on the products formed in this process from allylic peroxy-derivatives, since such compounds are known to give rise to epoxides[3-5] in these reactions as shown in Scheme 1.



7–14

1 Y = CMe_2OMe, R = Me, X = CO_2Et
2 Y = CMe_2Ph, R = Me, X = CO_2Et
3 Y = Bu^t, R = Me, X = CO_2Et
4 Y = Bu^t, R = H, X = H
5 Y = $SiMe_3$, R = Me, X = CO_2Et
[**6** = Bu^tO_2Ac]
7 Z = Me, R = Me, X = CO_2Et
8 Z = Me, R = H, X = H
9 Z = c-C_6H_{11}, R = Me, X = CO_2Et
10 Z = c-C_6H_{11}, R = H, X = H
11 Z = $(MeO_2C)_2CH$, R = Me, X = CO_2Et
12 Z = $(MeO_2C)_2CH$, R = H, X = H
13 Z = $MeO_2CCH_2CO_2CH_2$, R = Me, X = CO_2Et
14 Z = $MeO_2CCH_2CO_2CH_2$, R = H, X = H

Scheme 1 Mechanism of the reaction of induced decomposition of allylic peroxides

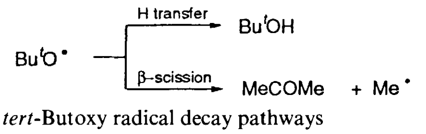
The mechanism of the reaction shows three different steps: production of radical Z$^\cdot$, addition of radical Z$^\cdot$ to the double bond and intramolecular homolytic substitution (S_Hi) on the O–O bond. Oxy radicals involved in the reaction are transformed generally by competitive processes such as hydrogen transfers, additions to unsaturations, or β-eliminations, mainly influenced by polar and steric factors.[6]

Our previous results[1,3,4] showed that the intramolecular homolytic substitution leading to epoxides is so fast a process that the radical adduct gives way generally only to this reaction and the nature of the solvent is unimportant, provided the latter is not a very efficient atom donor to a carbon centred radical, *e.g.* polyhalogenoalkanes.[7] Then, the formation of the epoxides will essentially depend on the two other reactions that we proposed to study. Thus, the peroxides **1**–**5** were designed as possessing various Y groups for the same acrylic unsaturation or the same group Y (Bu^t) for two different types of double bonds (electron-rich or -deficient). The possible reaction of the oxy radical YO$^\cdot$ with the solvent led to the use of cyclohexane, dimethyl malonate and benzene, defined according to the presence or absence of reactive hydrogens in these molecules and to the nucleophilicity of the radicals produced by the hydrogen abstractions. The reaction conditions were the same as those employed in the previous study on the induced decomposition of acrylic-type peroxides[1] (solvent:**1**–**5**:*tert*-butyl peracetate **6** = 20:1:0.1; 110 °C, 12 h).

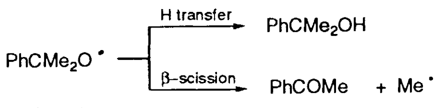
Results and Discussion

Before the presentation of the results dealing with the formation of the epoxides, the behaviour of the eliminated oxy radical YO$^\cdot$ will be analysed *via* its products of transformation. Indeed, one could see, from the mechanism of the reaction (Scheme 1), that the attacking radical Z$^\cdot$ depends upon the radical YO$^\cdot$ eliminated.

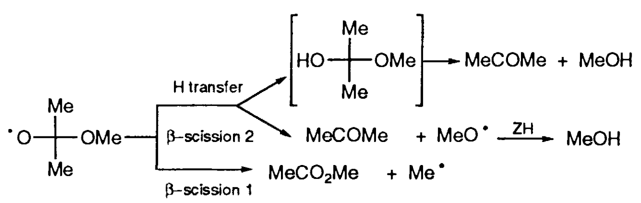
Reactions of the Oxy Radicals YO$^\cdot$.—The various products arising from the transformation of the YO moiety are essentially 'low boiling' compounds whose mechanisms of formation are described in Schemes 2–5. The two main transformations are



Scheme 2 *tert*-Butoxy radical decay pathways



Scheme 3 2-Phenylprop-2-yl radical decay pathways



Scheme 4 1-Methyl-1-methoxyethoxy radical decay pathways

$$Me_3SiO^\bullet \xrightarrow{\text{H-transfer}} [Me_3SiOH] \longrightarrow \tfrac{1}{2}\,Me_6Si_2O + \tfrac{1}{2}\,H_2O$$

Scheme 5 Trimethylsiloxy radical decay pathway

Table 1 Yields[a] of the products derived from OY moiety in the induced decomposition of the peroxy-derivatives **1–5** and thermolysis of **6** in cyclohexane

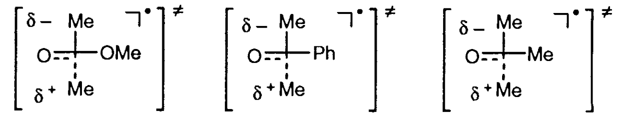
		Yield (%)		
Peroxide	$OY^\bullet$	'Alcohol'	'Carbonyl'	HTEC[d]
1	$^\bullet OCMe_2OMe$	2^b	95	2
2	$^\bullet OCMe_2Ph$	72	20	78
3	$^\bullet OBu^t$	86	5	94
4	$^\bullet OBu^t$	83	4	95
5	$^\bullet OSiMe_3$	98^c	—	100
6	$^\bullet OBu^t$	80	15	84

[a] GC yields relative to **1–5** and/or **6**. [b] As methanol and acetone. [c] As hexamethyldisiloxane. [d] Hydrogen transfer efficiency coefficient, HTEC = 100 × 'Alcohol'/('Alcohol' + 'Carbonyl').

hydrogen transfer to the solvent leading to the formation of an 'alcohol' and β-elimination with the formation of a 'carbonyl'. These primary products could get transformed in the medium in various ways. *tert*-Butanol was found to react partially with dimethyl malonate to produce the mixed diester as observed in a test reaction. 1-Methyl-1-phenylethanol was partially dehydrated to produce α-methylstyrene[8] and did not react by transesterification upon malonate as did *tert*-butanol. Trimethylsilanol was readily converted into hexamethyldisiloxane. 1-Methoxy-1-methylethanol spontaneously generated methanol and acetone which were titrated to determine the amount of the initially formed hemiketal. It has been reported that upon introduction of methyl radicals in benzene, some amount of toluene was produced by homolytic substitution on the aromatic solvents.[9]

Induced decomposition of peroxides **1–5** *in cyclohexane.* Table 1 summarizes the results of the study of the products derived from the oxy radicals $YO^\bullet$ generated by the decompositions of **1–5** in cyclohexane. This solvent is generally considered in free radical chemistry as a good hydrogen donor towards oxy radicals[10] since these electrophilic entities abstract hydrogen atoms efficiently from the high electron density sites. Except in the case of the radical $CH_3O(CH_3)_2CO^\bullet$, high values of hydrogen transfer efficiency coefficient (HTEC) are observed, with the highest number for the siloxy radical for which no β-scission occurred. The study of the products of thermolysis of *tert*-butyl peracetate **6** was also performed in this solvent with the view to reach the 'real' value of the abstraction efficiency of *tert*-butoxy radicals towards cyclohexane so as to compare them with the experimental HTEC values of **3** and **4** (Table 1). The higher HTEC values observed for **3** and **4** in contrast to that for **6** could be explained by a hydrogen abstraction at the allylic position of the unsaturated peroxide by the *tert*-butoxy radicals, as previously reported by our group.[11,12] The difference in the HTEC values determined for 2-phenylprop-2-yl and *tert*-butoxy radicals must be attributed, as pointed out earlier,[13–15] to a higher rate of β-scission in the case of the former. It is much more difficult to define if the observed reactivity of the 1-methoxy-1-methylethoxy radical in this respect, in comparison with these two oxy radicals, is caused by an enhanced rate of β-scission or by a decreased rate of hydrogen abstraction towards cyclohexane or even by a combination of both (Scheme 4).

According to the Hammond hypothesis[16] concerning an exothermic reaction, an early transition state would be involved in the elimination reaction. A polar mesomeric formula of the transition state, having similar structure to the radical, could be designed (Scheme 6). The stabilizing electron-withdrawing effect of the substituent on the carbon linked to the oxygen atom would imply the order of stabilization of the oxy radicals as: $(CH_3)_3CO^\bullet < Ph(CH_3)_2CO^\bullet < CH_3O(CH_3)_2CO^\bullet$.



Scheme 6 Polar mesomeric formulae of the transition state of β-scission of oxy radicals

Induced decomposition of peroxides **1–5** *in dimethyl malonate.* Table 2 describes the balance of the products generated from the YO moiety of the peroxy-compounds **1–5** decomposed in dimethyl malonate. The transformation of the radicals $YO^\bullet$ eliminated from peroxides **1** and **5** does not seem to change on replacing cyclohexane by dimethyl malonate. Conversely, *tert*-butoxy and 2-phenylprop-2-yloxy radicals abstracted hydrogen atoms to dimethyl malonate less efficiently, undergoing predominantly β-elimination. The comparison of the strengths of the different C–H bond in these solvents indicates that this behaviour could not be attributed to thermodynamic reasons: E_{C-H}(cyclohexane) = 401 kJ mol^{-1},[17] E_{C-H}(CH_2, dimethyl malonate) = 385 kJ mol^{-1},[18] E_{C-H}(CH_3, dimethyl malonate) = 418 kJ mol^{-1}.[18]

As pointed out earlier in the case of cyclohexane, different HTEC values for **3**, **4** and **6** indicate the peroxide as another source of hydrogen at least for the decomposition of the second derivative in dimethyl malonate. In order to define the relative importance of these secondary reactions, the induced decomposition of both unsaturated peroxides was performed using various molar ratios of the reactants (Table 3). One could see that in both cases HTEC values are close to 22%, for the lower concentration of peroxide, which could be considered as the exact value of the efficiency of hydrogen abstraction from dimethyl malonate by *tert*-butoxy radicals. The higher value obtained in the case of *tert*-butyl peracetate could be explained by a hydrogen abstraction from this initiator since its decomposition was performed at higher concentration. The incomplete balance of the *tert*-butoxy moiety could be certainly attributed to the existence of cage reactions in the thermolysis of the perester[19] or to the 'ionic' decomposition of the perester[20] in this slightly polar solvent.

Induced decomposition of peroxides **1–5** *in benzene.* Table 4 summarizes the yields of the compounds produced by the reaction of the various $YO^\bullet$ species formed in the induced decomposition of compounds **1–5** and thermolysis of **6** in benzene. Besides the expected reaction products of the various oxy radicals, 'alcohol' and 'carbonyl', toluene was also identified but in very low amounts for peroxides **1–5**. Since benzene is an inefficient hydrogen donor to radicals, the yields of 'alcohols' indicate that the peroxide underwent important allylic hydrogen abstraction by oxy radicals (Scheme 7), confirming the previous results.[11,12] Indeed, blank experiments proved that the produced epoxides are not involved in hydrogen transfer

Table 2 Yields[a] of the products derived from OY moiety in the induced decomposition of the peroxy-derivatives **1**–**5** and thermolysis of **6** in dimethyl malonate

Peroxide	OY$^{\bullet}$	Yield (%)			
		'Alcohol'	'Carbonyl'	$\mathrm{MeO_2CH_2CO_2R}$	HTEC[e]
1	$^{\bullet}\mathrm{OCMe_2OMe}$	2[b]	98	—	2
2	$^{\bullet}\mathrm{OCMe_2Ph}$	2[c]	80	—	20
3	$^{\bullet}\mathrm{OBu}^t$	11	67	22	33
4	$^{\bullet}\mathrm{OBu}^t$	14	60	26	40
5	$^{\bullet}\mathrm{OSiMe_3}$	90[d]	—	—	100
6	$^{\bullet}\mathrm{OBu}^t$	7	58	18	30

[a] GC yields relative to **1**–**5** and/or **6**. [b] As methanol and acetone. [c] Remaining alcohol (for calculation of HTEC, a yield of 20% was assumed). [d] As hexamethyldisiloxane. [e] Hydrogen transfer efficiency coefficient, HTEC = 100 x 'Alcohol'/('Alcohol' + 'Carbonyl').

Table 3 Yields[a] of the products formed in the reaction of *tert*-butoxy radicals arising from peroxidic compounds **3** and **4** in dimethyl malonate

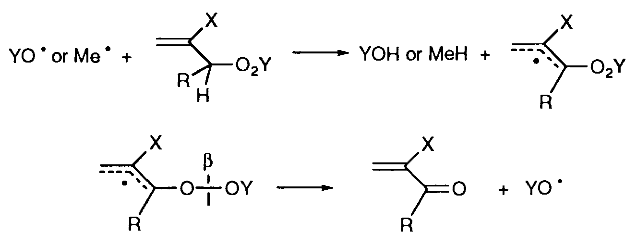
Peroxide	$\mathrm{(MeO_2C)_2CH}$: **3** or **4**[b]	Yield (%)			
		$\mathrm{Me_2CO}$	$\mathrm{Bu}^t\mathrm{OH}$	$\mathrm{MeO_2CCH_2CO_2Bu}^t$	HTEC[c]
3	20	67	11	22	33
	50	72	6	22	28
	100	76	3	21	24
	200	78	2	20	22
4	20	60	14	26	40
	50	68	7	25	32
	100	75	4	21	25
	200	78	3	19	22

[a] GC yields relative to **3** and **4**. [b] Molar ratio. [c] Hydrogen transfer efficiency coefficient, HTEC = 100 x 'Alcohol' ('Alcohol' + 'Carbonyl').

Table 4 Yields[a] of the products arising from OY moiety in the induced decomposition of the peroxy-derivatives **1**–**5** and thermolysis of **6** in benzene

Peroxide	$^{\bullet}$OY	Yield (%)			
		'Alcohol'	'Carbonyl'	Toluene	HTEC[d]
1	$^{\bullet}\mathrm{OCMe_2OMe}$	2[b]	97	—	2
2	$^{\bullet}\mathrm{OCMe_2Ph}$	8	87	3	8
3	$^{\bullet}\mathrm{OBu}^t$	22	70	3	24
4	$^{\bullet}\mathrm{OBu}^t$	50	36	4	58
5	$^{\bullet}\mathrm{OSiMe_3}$	92[c]	—	—	100
6	$^{\bullet}\mathrm{OBu}^t$	36	53	32	40

[a] GC yields relative to **1**–**5** and/or **6**. [b] As acetone and methanol. [c] As hexamethyldisiloxane. [d] Hydrogen transfer efficiency coefficient, HTEC = 'Alcohol'/('Alcohol' + 'Carbonyl').



Scheme 7 Induced decomposition of peroxides **1**–**5** due to allylic hydrogen abstraction

Table 5 Yields[a] of the products formed in the reaction of *tert*-butoxy radicals produced in the induced decomposition of **4** and the ethyl *tert*-butyldioxymethylpropenoate in benzene

Peroxide	Yield (%)		
	$\mathrm{Me_2CO}$	$\mathrm{Bu}^t\mathrm{OH}$	PhMe
$\mathrm{EtO_2CC({=}CH_2)CH_2O_2Bu}^t$[b]	52	38	3
$\mathrm{H_2C{=}CHCH_2O_2Bu}^t$	50	36	4

[a] GC yields relative to peroxides. [b] Ref. 11.

reactions to alkoxy radicals. On the other hand, the low amount of toluene showed that cyclohexadienyl radicals could not be invoked for an efficient hydrogen transfer as in the case of the thermolysis of compounds **6** in such a solvent (Table 4).

The comparison of the yields of formation of *tert*-butanol and acetone produced in the induced decomposition of peroxides **4** and ethyl 2-*tert*-butyldioxymethylpropenoate,[11] summarized in Table 5, shows that the presence of an ester group conjugated with the double bond has no significant effect on the allylic hydrogen abstraction.

Free Radical Additions to the Double Bond of the Unsaturated Peroxidic Derivatives.—The induced decomposition of the peroxy-compound is highly dependent on the first step of the chain reaction (the formation of the radical Z$^{\bullet}$ by abstraction of hydrogen from the solvent). The free radical addition to the double bond of unsaturated peroxides was also examined by analyses of the epoxides produced. Indeed, according to the nature of the radical Z$^{\bullet}$ and of the double bond of the peroxide, addition reaction could be favoured or disfavoured by polar effects.[21] Similar effects will also play a role in the competitive

Table 6 Yields[a] of epoxides produced in the induced decomposition of **1**–**5** in cyclohexane

Peroxide	$^\bullet$OY	Yield (%) 7 or 8[b]	9 or 10[c]	Allylic attack[d]
1	$^\bullet$OCMe$_2$OMe	77	16	7
2	$^\bullet$OCMe$_2$Ph	20	70	10
3	$^\bullet$OBu^t	5	84	11
5	$^\bullet$OSiMe$_3$	—	83	17
4	$^\bullet$OBu^t	2	66	32

[a] GC yields relative to **1**–**5**. [b] Me$^\bullet$ addition. [c] c-$C_6H_{11}{}^\bullet$ addition. [d] Estimation of allylic attack. Calculated as: 100% − (%**7** or **8**) − (%**9** or **10**).

Table 7 Yields[a] of epoxides produced in the induced decomposition of **1** and **3** in cyclohexane

Peroxide	c-C_6H_{12}:**1**[b]	Yield (%) 7[c]	9[d]	Allylic attack[e]
1	20	77	16	7
	50	62	35	3
	100	48	52	—
	200	35	65	—
3	20	5	84	11
	50	4	92	4
	100	3	96	1
	200	2	98	—

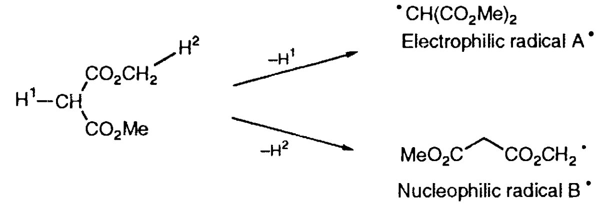
[a] GC yields relative to **1** or **3**. [b] Molar ratio. [c] Me$^\bullet$ addition. [d] c-$C_6H_{11}{}^\bullet$ addition. [e] Estimation of allylic attack. Calculated as: 100% − (%**7**) − (%**9**).

side reactions of $CH_3{}^\bullet$, addition to the double bond or hydrogen abstraction to the solvent.

Induced decomposition of peroxides **1**–**5** *in cyclohexane.* The results obtained in the induced decompositions of the peroxides **1**–**5** in cyclohexane (Table 6) were analysed taking into account the various reactions of the different oxy and alkyl radicals produced in the medium. Epoxide **9** or **10** was the main product when the preferential decay of the oxy radical was by way of hydrogen abstraction from cyclohexane, as was general in all cases, except by the peroxyketal **1**. The formation of epoxide **7** as the major product of the induced decomposition of **1** indicates that methyl radicals preferred to add to the double bond of the unsaturated peroxyketal rather than decaying by way of abstracting a hydrogen from cyclohexane. Comparison of the yields of epoxide **9** (Table 6) and of methanol and acetone (Table 1) proved that cyclohexyl radicals were essentially produced in the reaction of methyl radicals with cyclohexane. This hypothesis was confirmed by the determination of the influence of the molar ratios of the reactants on the yields of both epoxides **7** and **9** (Table 7). Nevertheless, one could see that even at low concentration it is impossible to direct the reaction towards the sole formation of **9**.

The addition of the nucleophilic cyclohexyl and methyl radicals to the electron-deficient double bond of the acrylic peroxide **3** appeared much more favoured than the addition to the allylic peroxide **4** possessing an electron rich double bond. Nevertheless, the formation of epoxide **10** with a fair yield confirmed that there is no inhibition of the addition of an alkyl radical to the double bond of alkenyl peroxide as pointed out earlier.[3] The difference in the yield of corresponding epoxides in the two cases could certainly be attributed to a more facile allylic attack in the case of peroxide **3** than in the case of **4**. The determination of the rate of spontaneous decomposition of both peroxides using a DSC method[12] showed that these peroxides were not disappearing *via* the direct homolysis of the O–O bond. Then, assuming that these compounds were consumed only by homolytic induced decomposition either *via* the process involving the addition of methyl and cyclohexyl radicals or *via* allylic hydrogen abstraction followed by β-elimination, an estimation of the extent of allylic attack could be done (Table 6). The results presented for peroxide **3** in Table 7 are in agreement with this hypothesis since an increase of the molar ratio cyclohexane:**1** or **3** favoured the formation of epoxides and below a value of 100:1 no allylic attack seemed to occur. The comparison of the values of the estimated allylic attacks for the various compounds (Table 6) showed that for the same kind of allylic hydrogen in the acrylic compounds (**1**, **2**, **3**, **5**) there is an apparent relationship between the importance of this reaction and the efficiency of hydrogen abstraction of the oxy radical produced in the S_Hi (Tables 1 and 6). This would imply that the oxy radicals are more prone to abstract allylic hydrogens than the alkyl radicals. However, the analysis of the results obtained with the peroxyketal **1** (Tables 6 and 7) shows that alkyl radicals were also involved in such a reaction. Considering the 'dilution effect' (Table 7) one could exclude the possibility for the degradation of the peroxide in cyclohexane by allylic attack (molar ratio cyclohexane:**1** = 100 and cyclohexane:**3** = 200).

Induced decomposition of peroxides **1**–**5** *in dimethyl malonate.* Dimethyl malonate could undergo two types of hydrogen abstraction to yield two different radicals of opposite nucleophilicity (Scheme 8). Table 8 summarizes the yields of formation of the corresponding epoxides **11** or **12** (addition of radical A$^\bullet$) and **13** or **14** (addition of radical B$^\bullet$) and **7** (addition of $CH_3{}^\bullet$). A direct analysis of the results described in Table 8 is rather difficult if we consider the different decay paths of the eliminated oxy radicals. In order to facilitate it, we are going to study, first of all, the induced decompositions of peroxides **1** and **5**. Indeed, in such reactions methyl and trimethylsiloxy radicals, respectively, are the only radicals involved in the generation of the radicals Z$^\bullet$ responsible for the induced decomposition of these peroxides. The formation of epoxide **13**, in the induced decomposition of peroxide **5**, is in agreement with the expected influence of polar effects: in the hydrogen abstraction from dimethyl malonate by trimethylsiloxy radicals; and in the addition of the nucleophilic radicals B$^\bullet$ to the electron-deficient double bond of peroxide **5**. Nevertheless, the observation of epoxide **11** indicates the existence of radicals A$^\bullet$ in the medium. They could have several origins: direct hydrogen abstraction from dimethyl malonate by trimethylsiloxy radicals or by *tert*-butoxy and methyl radicals produced in the spontaneous decomposition of the initiator **6**; or, generation of radical B$^\bullet$ by hydrogen abstraction from the diester by radical A$^\bullet$ used as solvent as previously noticed in the case of monoesters.[22]



Scheme 8 Hydrogen abstraction from dimethyl malonate

In order to eliminate the production of *tert*-butoxy and methyl radicals, initiation was performed using α,α'-azobisisobutyronitrile (AIBN) in similar conditions (110 °C). The electrophilic radicals $^\bullet C(CH_3)_2CN$ are not involved in the abstraction step since only traces of isobutyronitrile were identified in the reaction products. The two epoxides **11** and **13** were also obtained under such initiation conditions. Induced decompositions of **5** in dimethyl malonate, realized with different molar ratios of dimethyl malonate and **5**, gave similar

Table 8 Yields[a] of epoxides produced in the induced decomposition of unsaturated peroxides **1**–**5** in dimethyl malonate

Peroxide	$^{\bullet}$OY	Yield (%) **7** or **8**[b]	**11** or **12**[c]	**13** or **14**[d]	Allylic attack[e]
1	$^{\bullet}OCMe_2OMe$	78	13	2	7
2	$^{\bullet}OCMe_2Ph$	64	17	7	12
3	$^{\bullet}OBu^t$	57	14	16	13
5	$^{\bullet}OSiMe_3$	—	16	37	47
4	$^{\bullet}OBu^t$	11	40	5	44

[a] GC yields relative to **1**–**5**. [b] Me$^{\bullet}$ addition. [c] A$^{\bullet}$ addition. [d] B$^{\bullet}$ addition. [e] Estimation of allylic attack. Calculated as: 100% − (%**7** or **8**) − (%**11** or **12**) − (%**13** or **14**).

Table 9 Yields[a] of epoxides produced in the induced decomposition of **1** in dimethyl malonate

$(MeO_2C)_2CH_2$:**1**[b]	Yield (%) **7**[c]	**11**[d]	**13**[e]	Allylic attack[f]
20	78	13	2	7
50	65	30	2	3
100	56	40	2	2
200	50	48	2	—

[a] GC yields relative to **1**. [b] Molar ratio. [c] Me$^{\bullet}$ addition. [d] A$^{\bullet}$ addition. [e] B$^{\bullet}$ addition. [f] Estimation of allylic attack. Calculated as 100% − (%**7**) − (%**11**) − (%**13**).

Table 10 Yields[a] of epoxides produced in the induced decomposition of **3** in dimethyl malonate

$(MeO_2C)_2CH_2$:**3**[b]	Yield (%) **7**[c]	**11**[d]	**13**[e]	Allylic attack[f]
20	57	14	16	13
50	47	27	20	6
100	37	38	22	3
200	31	46	22	1

[a] GC yields relative to **3**. [b] Molar ratio. [c] Me$^{\bullet}$ addition. [d] A$^{\bullet}$ addition. [e] B$^{\bullet}$ addition. [f] Estimation of allylic attack. Calculated as 100% −(%**7**) − (%**11**) − (%**13**).

Table 11 Yields[a] of epoxides produced in the induced decomposition of **4** in dimethyl malonate

$(MeO_2C)_2CH_2$:**4**[b]	Yield (%) **8**[c]	**12**[d]	**14**[e]	Allylic attack[f]
20	11	40	5	44
50	8	57	10	25
100	5	69	13	13
200	3	75	15	7

[a] GC yields relative to **4**. [b] Molar ratio. [c] Me$^{\bullet}$ addition. [d] A$^{\bullet}$ addition. [e] B$^{\bullet}$ addition. [f] Estimation of allylic attack. Calculated as 100% − (%**8**) − (%**12**) − (%**14**).

values for the relative quantities of epoxides **11** and **13**. This study proves that there is no hydrogen abstraction from the solvent by A$^{\bullet}$ to generate B$^{\bullet}$ in the conditions of the study. These two last experiments are then confirming the ability of trimethylsiloxy radicals to abstract a hydrogen from dimethyl malonate in both reactive positions. The major product of the induced decomposition of peroxide **1** is epoxide **7**, as observed when the solvent was cyclohexane. Besides this compound, two other epoxides, **11** and **13**, formed respectively by addition of radicals A$^{\bullet}$ and B$^{\bullet}$ to **1**, were identified. The relative ratio of the reactants (dimethyl malonate:**1**) is an important factor for the composition of the epoxide mixture, as shown in Table 9, even if it was impossible to direct the reaction exclusively toward the formation of epoxide **11**.

The increasing amount of the single epoxide **11** with increase in the molar ratio dimethyl malonate:**1** indicates a regiospecific attack of methyl radicals on dimethyl malonate agreeing with the regioselectivity observed in the free radical alkylation of dialkyl malonates by alkenes.[21] Epoxide **13**, arising from the addition of radicals B$^{\bullet}$ to **1**, results certainly from a hydrogen abstraction from the diester by alkoxy radicals, which can be either *tert*-butoxy produced in the homolysis of the initiator **6** or by $CH_3O(CH_3)_2CO^{\bullet}$ generated in the S_Hi reaction, or methoxy formed by β-elimination from the latter.

The results observed for the two other 'acrylic' peroxides **2** and **3** are intermediate between **1** and **5**. This is not surprising if we consider the reactive pathway of *tert*-butoxy and 2-phenylprop-2-yloxy radicals (the eliminated oxy radical is reacting either by hydrogen abstraction from the dimethyl malonate or β-elimination generating methyl radicals). Then, these results have to be analysed as the combination of the various reactions of methyl and *tert*-alkoxy radicals (whose reactivity in hydrogen abstraction would be similar to that of trimethylsiloxy radicals).

The comparison of the induced decompositions of **3** and **4** (Table 8) indicates that, although the radical eliminated in the S_Hi is the same, the yields of the homologous epoxides (**7** and **8**, **11** and **12**, **13** and **14**) produced are very different. Assuming a similar behaviour for the *tert*-butoxy radicals in these conditions (Table 2), one could see that the electron-rich double bond of peroxide **4** prefers to be attacked by the electrophilic radicals A$^{\bullet}$ than by the nucleophilic radicals B$^{\bullet}$ and methyl, conversely to the electron-poor one of peroxide **3**. Unsuccessful attempts of dilution were performed in order to see if the induced decomposition of these peroxides could be synthetically interesting with the selective formation of a single epoxide (Tables 10 and 11). It is worthwhile to underline, in the work of Roberts and Dang,[5] the efficiency of the induced decomposition of allylic peroxides by radical generated from malonates to yield selectively epoxides resulting from the attack of the double bond by radicals homologous of A$^{\bullet}$. Such a selectivity was obtained by operating at 30 °C, instead of at 110 °C, using amine-boranes as polarity reversed catalysts.

The proportion of peroxide **1**–**5** disappearing by allylic attack (Table 8) was estimated as in the case of reaction performed in cyclohexane. A similar conclusion on an apparent relationship between the allylic attack and the hydrogen abstraction efficiency of oxy radical produced in the S_Hi (Tables 2 and 8) could be reached. However, allylic attack appears to be more important in the case of reactions performed in dimethyl malonate. This observation is in good agreement with an apparent lower lability of hydrogens of this solvent towards abstraction by oxy radical (Tables 1 and 2). These results are confirmed by attempts of dilution indicating that, conversely to

Table 12 Yield[a] of epoxides produced in the induced decomposition of **1**–**5** in benzene

Peroxide	˙OY	Yield (%) 7 or 8	Yield (%) Allylic attack[b]
1	˙OCMe$_2$OMe	92	8
2	˙OCMe$_2$Ph	83	17
3	˙OBu^t	67	33
5	˙OSiMe$_3$	—	100
4	˙OBu^t	14	86

[a] GC yields relative to **1**–**5**. [b] Estimation of allylic attack. Calculated as: 100% − (%**7** or **8**).

Table 13 NMR analyses of the residue originated from induced decomposition of **3** in benzene

δ_H	δ_C
0.9–1.4 (CH$_3$)	13–22 (CH$_2$ and CH$_3$)
1.4–2 (CH and CH$_2$)	29–30 (C α to C=O)
2–2.4 (H α to C=O and epoxidic H)	55–72 (C, CH$_2$ and CH α to O)
4–4.3 (CH$_2$-O of ester)	126–129 (ArC)
7–7.5 (ArH)	170 (C=O ester)
	205 (C=O ketone)

the reactions performed in cyclohexane it was impossible to eliminate this secondary reaction even with molar ratios of dimethyl malonate to **1**, **3** or **4** as high as 200.

Induced decomposition of peroxides **1**–**5** *in benzene.* Table 12 summarizes the results observed in the induced decomposition of peroxides **1**–**5** in benzene. A single epoxide corresponding to the addition of methyl radical to the unsaturation (**7** and **8**) was identified. The amounts of epoxide **7** agree with the yields of the 'carbonyl' produced in the β-scission of the oxy radicals (Table 3), indicating that the main reaction of the methyl radical in benzenic solutions of 'acrylic' peroxides is the addition to the double bond. Conversely, these radicals, produced from allyl *tert*-butyl peroxide **4**, have some other decay paths (certainly allylic attack) since only some of them are adding to the unsaturation (Tables 3 and 12). These observations totally conform with the expected polar effects in methyl radical addition to an electron-rich double bond. In the case of trimethylsilyl peroxide **5**, absence of epoxide **7** was noticed confirming that these radicals do not degrade by β-scission. ^{1}H and ^{13}C NMR analyses of the various residues obtained after elimination of the volatile compounds were performed as previously[11] in the case of the induced decomposition of ethyl 2-*tert*-butyldioxymethylpropenoate, confirming that ethyl poly-(2-acetylacrylate) was the main component of the residue (*e.g.* in the case of **3** in Table 13).

Conclusions

This study on the induced decomposition of various unsaturated peroxides indicated that the production of epoxides by these reactions is highly dependent on three parameters: the nature of the leaving oxy radicals and their decay paths (β-scission, hydrogen abstraction from the solvent or allylic hydrogen abstraction from the peroxy-derivative), the ability of the solvent to give hydrogen to oxy and alkyl radicals and the nature of the radical attacking the double bond to provoke the induced decomposition of the peroxide.

It was shown that the rules of the free radical reactions, particularly hydrogen abstraction from a substrate and addition to an unsaturation, govern the induced decomposition of these unsaturated peroxides and must be combined to anticipate the compounds produced. Thus, depending on the target compound, several peroxy-derivatives and/or processes could be designed to realize its synthesis. Unsaturated peroxy-derivatives were found to undergo significant induced decomposition by way of allylic attack (whenever possible) by oxy radicals. Such a phenomenon and the low selectivity of these radicals in hydrogen abstractions imply the need to define new ways of selective production of alkyl radicals to make these reactions useful for synthesis, which is the main purpose of our present research.

Experimental

^{1}H NMR spectra were recorded at 250 MHz and the ^{13}C NMR data obtained at 62.9 MHz on a Bruker AC 250 spectrometer from CDCl$_3$ solution of the compounds. ^{1}H And ^{13}C NMR chemical shifts of major diastereoisomer(s) are in bold typeface (when known). Elemental analyses were performed at the *Laboratoire Central de Microanalyse* (CNRS), Vernaison, France. All column chromatographic separations were carried out on Merck silica gel 60 (60–200 mesh). Evaporative distillation refers to flask-to-flask distillation under reduced pressure using a Büchi Kugelrohr oven. Light petroleum was distilled (b.p. 40–60 °C) whereas cyclohexane and benzene were reagent grade and just dried prior to use. Dimethyl malonate was distilled and stored over molecular sieves 4 Å.

Ethyl 3-tert-*Butyldioxy-2-methylenebutanoate* **3**.—To a stirred solution of ethyl 2-bromomethylbut-2-enoate[23] (20.7 g, 0.1 mol), *tert*-butyl hydroperoxide, purity 90% (11 g, 0.11 mol) and poly(ethylene oxide) (1 g) in distilled tetrahydrofuran (100 cm^3) was added in small portions commercially available KOH, 85% pure (7.25 g, 0.11 mol) over 1 h. Stirring was continued for 2 h, the reaction mixture being allowed to warm to room temperature. The solvent was then evaporated under reduced pressure and water (10 cm^3) was added to the residue. The mixture was extracted three times with distilled light petroleum (30 cm^3), washed with a saturated aqueous NaCl and the combined organic layers were dried (MgSO$_4$). After elimination of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel (8.28 g, 45%); R_f = 0.45, light petroleum–Et$_2$O = 95:5; δ_H 6.23 (m, 1 H), 5.86 (m, 1 H), 4.80 (q, *J* 6.5, 1 H, CH$_3$C*H*), 4.15 (q, *J* 7.1, 2 H, CO$_2$C*H*$_2$), 1.25–1.19 (m, 6 H, C*H*$_3$CH and CH$_2$C*H*$_3$) and 1.14 [s, 9 H, C(CH$_3$)$_3$]; δ_C 166.0, 141.2, 124.9, 80.0, 77.3, 60.5, 26.3, 18.3 and 14.1 (Found: C, 61.0; H, 28.9. C$_{11}$H$_{20}$O$_4$ requires C, 61.1; H, 29.6%).

Allyl tert-*Butyl Peroxide* **4**.—This was prepared from allyl bromide and the *tert*-butyl hydroperoxide under phase transfer conditions.[24]

Ethyl 3-(2-*Phenylprop-2-yldioxy*)-2-*methylenebutanoate* **2**.—This compound was prepared according to the procedure used for **7** (6.89 g, 28%); R_f = 0.39, light petroleum–Et$_2$O = 95:5; δ_H 7.52–7.25 (m, 5 H, Ph), 6.35 (m, 1 H), 5.97 (m, 1 H), 5.0 (q, *J* 6.5, 1 H, CH$_3$C*H*), 4.24 (q, *J* 7.1, 2 H, CO$_2$CH$_2$), 1.65 (s, 3 H, CH$_3$), 1.61 (s, 3 H, CH$_3$), 1.33 (d, *J* 6.5, 3 H, C*H*$_3$CH) and 1.27 (t, *J* 7.1, 3 H, CH$_2$C*H*$_3$); δ_C 166.1, 145.5, 141.3, 128.0, 125.5, 127.0, 125.0, 82.9, 77.5, 60.6, 26.9, 26.4, 18.9 and 14.2 (Found: C, 68.9; H, 7.8. C$_{16}$H$_{22}$O$_4$ requires C, 69.05; H, 7.95%).

Ethyl 3-(2-*Methoxyprop-2-yldioxy*)-2-*methylenebutanoate* **1**.—To a cooled (−10 °C) solution of ethyl 3-hydroperoxy-2-methylenebutanoate[25] (4.8 g, 30 mmol) and toluene-*p*-sulfonic acid monohydrate (50 mg, 0.2 mmol) in Et$_2$O (50 cm^3), a solution of 2-methoxypropene (2.16 g, 30 mmol) in Et$_2$O (10 cm^3) was added dropwise under stirring. The stirred reaction mixture was then allowed to warm slowly at room temperature, and then washed with aqueous Na_2CO_3 (10 cm^3) and water (2 × 10 cm^3). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure and the product purified by flash chromatography on a column of silica gel (5.63 g, 81%); R_f = 0.37, light petroleum–Et_2O = 88 : 12; δ_H 6.27 (s, 1 H), 5.90 (s, 1 H), 4.93 (q, *J* 6.6, 1 H, CH_3CH), 4.16 (q, *J* 7.1, 2 H, CO_2CH_2), 3.22 (s, 3 H, OCH_3) and 1.34–1.21 (m, 12 H); δ_C 165.9, 141.2, 124.9, 104.6, 77.6, 60.6, 49.1, 22.8, 22.6, 18.7 and 14.1 (Found: C, 56.8; H, 8.75. $C_{11}H_{20}O_5$ requires C, 56.88; H, 8.68%).

Ethyl 2-*Methylene*-3-*trimethylsilyldioxybutanoate* **5**.—This peroxysilane was prepared by a general method described by Buncel and Davies.[26] To a stirred solution of pyridine (1.58 g, 0.02 mol) in light petroleum (20 cm^3), trimethylsilyl chloride (2.17 g, 0.02 mol) was added dropwise. The stirred reaction mixture was then cooled to – 10 °C and a solution of ethyl 3-hydroperoxy-2-methylenebutanoate[25] (2.56 g, 0.02 mol) in light petroleum (5 cm^3) was added dropwise. The medium 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 reduced pressure, the peroxysilane was flask-to-flask distilled (3.5 g, 90%), T_{oven} 55 °C/0.1 Torr;* δ_H 6.37 (m, 1 H), 5.94 (m, 1 H), 4.91 (q, *J* 6.6, 1 H, CH_3CH), 4.22 (q, *J* 7.1, 2 H, CO_2CH_2), 1.3 (d, *J* 6.6, 3 H, CH_3CH), 1.28 (t, *J* 7.1, 3 H) and 0.17 (s, 9 H, $SiMe_3$); δ_C 165.9, 140.7, 125.3, 79.1, 60.7, 18.7, 14.1 and 1.4. (Found: C, 51.6; H, 8.75. $C_{10}H_{20}O_5Si$ requires C, 51.69; H, 8.68%).

Compounds **7**–**14**.—*General procedure*. A mixture of peroxide (20 mmol), *tert*-butyl peracetate **6** (0.26 g, 2 mmol) and solvent (200 mmol) were placed in an ampoule sealed under reduced pressure (10^{-3} Torr). After 12 h at 110 °C, the volatiles were removed under reduced pressure and the glycidic ester was distilled with a flask-to-flask apparatus.

Ethyl 2,3-*epoxy*-2-*ethylbutanoate* **7**. T_{oven} 90 °C/25 Torr (lit.,[27] 88–90 °C/20 Torr); δ_H 4.2 (m, 2 H, CO_2CH_2), 3.21 (q, *J* 5.5, 1 H, CH_3CH), 1.77 (ABX_3, J_{AB} 14.7, J_{AX} 7.4, 2 H, CH_3CH_2), 1.29 (*d*, *J* 5.5, 3 H, CH_3CH), 1.22 (t, *J* 7.1, 3 H, $CO_2CH_2CH_3$) and 1.01 (J_{AX} 7.4, 3 H, CH_3CH_2); δ_C 171.0, 169.5, 64.1, 61.7, 61.3, 61.2, 58.4, 58.3, 26.2, 20.8, 14.3, 14.1, 13.7, 13.5, 9.4 and 8.7.

1,2-*Epoxybutane* **8**. A commercial product (Aldrich).

Ethyl 2-*cyclohexylmethyl*-2,3-*epoxybutanoate* **9**. T_{oven} 90 °C/0.01 Torr; δ_H 4.2 (m, 2 H, CO_2CH_2), **3.08**, 2.92 (q, *J* 5.5, 1 H, CH_3CH) and 2.08–0.87 (m, 19 H); δ_C **171.6**, 170.1, **61.2**, 61.1, 62.5, **60.2**, 58.3, **57.4**, 35.0, **34.9**, 40.7, **34.1**, **33.4**, **33.3**, 33.2, **26.2**, **26.1**, **26.0**, 14.2, **14.0** and 13.8 (Found: C, 68.9; H, 9.78. $C_{13}H_{22}O_3$ requires C, 68.99; H, 9.80%).

3-*Cyclohexyl*-1,2-*epoxypropane* **10**. T_{oven} 85–87 °C/25 Torr (lit.,[28] 55–56 °C/2 Torr); δ_H 3.1–2.1 (m, 3 H) and 2.1–0.4 (m, 13 H); δ_C 50.3, 46.4, 40.7, 36.2, 33.8, 33.4, 26.7 and 26.5.

Dimethyl 2,3-*epoxy*-2-*ethoxycarbonylbutylmalonate* **11**. T_{oven} 110 °C/0.02 Torr; δ_H 4.1 (q, *J* 7.0, 2 H, CO_2CH_2), 3.63 (s d, 6 H, CO_2CH_3), 3.3 (m, 1 H, CH), **3.20**, 3.05 (q, *J* 5.0, 1 H, $CHCH_3$), 2.8–1.8 (m, 2 H, $CHCH_2$), 1.3 (d, *J* 5.0, 3 H, $CHCH_3$) and 1.2 (t, *J* 7.0, 3 H, $CO_2CH_2CH_3$); δ_C **170.1**, **169.2**, **168.9**, 167.2, 166.7, 166.2, **61.8**, 61.7, 60.5, **58.5**, 59.4, **58.7**, **52.6**, **52.5**, 52.3, **47.9**, 47.5, 31.7, **26.1**, 14.1, **13.9**, 13.5 and **13.3** (Found: C, 52.5; H, 6.7. $C_{12}H_{18}O_7$ requires C, 52.55; H, 6.62%).

Dimethyl 2,3-*epoxypropylmalonate* **12**. T_{oven} 65 °C/0.1 Torr (lit.,[28] 70 °C/0.25 Torr); δ_H 3.57 (s, 6 H, CO_2CH_3), 3.40 (br t, 1 H, CH), 2.85–2.3 (m, 3 H, H_{cycle}) and 2.14–1.74 (m, 2 H, $CHCH_2CH$); δ_C 169.1, 169.0, 52.5, 52.4, 49.5, 48.4, 46.8 and 31.6.

Methyl 3,4-*epoxy*-3-*ethoxycarbonylpentyl malonate* **13**. T_{oven} 120 °C/0.01 Torr; δ_H 4.2 (m, 2 H, CO_2CH_2), 4.09 (q, *J* 7.1, 2 H, CO_2CH_2), 3.62 (s, 3 H, OCH_3), 3.26 (s, 2 H, $O_2CCH_2CO_2$), **3.18**, 3.00 (q, *J* 5.5, 1 H, $CHCH_3$), 2.44–1.74 (m, 2 H, CH_2), **1.30**, 1.25 (d, *J* 5.5, 3 H, $CHCH_3$), **1.17** and 1.07 (t, *J* 7.1, 3 H, $CO_2CH_2CH_3$); δ_C **170.3**, 169.0, **166.7**, 166.4, **166.2**, 165.8, **63.5**, 63.2, **63.3**, 63.0, 60.4, **58.2**, 58.4, **58.0**, 52.4, 41.1, 32.0, **26.6**, 14.2, **14.0**, **13.6** and 13.4 (Found: C, 52.5; H, 8.7. $C_{12}H_{18}O_7$ requires C, 52.55; H, 6.62%).

3,4-*Epoxybutyl methyl malonate* **14**. T_{oven} 75 °C/0.3 Torr; δ_H 4.10 (t, *J* 6.2, 2 H, CO_2CH_2), 3.54 (s, 3 H, OCH_3), 3.22 (s, 2 H, CH_2), 2.82–2.80 (m, 1 H, CH_{cycle}), 2.58–2.30 (m, 2 H, CH_{2cycle}) and 1.83–1.56 (m, 2 H, $CO_2CH_2CH_2$); δ_C 166.8, 166.2, 62.2, 52.2, 49.1, 46.5, 41.0 and 31.5 (Found: C, 51.1; H, 6.4. $C_8H_{12}O_5$ requires C, 51.06; H, 6.43%).

Acknowledgements

The authors acknowledge Akzo Chemicals for a fellowship to one of us (D. C.) and Dr. A. J. De Jongh, Dr. P. Hope and Dr. J. Meijer (Akzo Chemicals Deventer) for very fruitful discussions during the course of this study.

References

1 Part 21, C. Navarro, M. Degueil-Castaing, D. Colombani and B. Maillard, *Synlett*, 1992, 587.
2 B. Maillard, X. Lubeigt and E. Montaudon, *Can. J. Chem.*, in the press.
3 E. Montaudon, F. Rakotomanana and B. Maillard, *Tetrahedron*, 1985, **41**, 2727; B. Maillard, E. Montaudon, F. Rakotomanana and M. J. Bourgeois, *Tetrahedron*, 1985, **41**, 5039; E. Montaudon, F. Rakotomanana and B. Maillard, *Bull. Soc. Chim. Fr.*, 1985, 198; B. Maillard, A. Kharrat, F. Rakotomanana, E. Montaudon and C. Gardrat, *Tetrahedron*, 1985, **41**, 4047; E. Montaudon, F. Rakotomanana and B. Maillard, *Bull. Soc. Chim. Fr.*, 1987, 375; B. Maillard, M. J. Bourgeois, R. Lalande and E. Montaudon, in NATO ASI Ser., *Free Radicals in Synthesis and Biology*, ed. F. Minisci, Kluwer Academic Publ., New York, 1989, **260**, p. 283; X. Lubeigt, F. Flies, M. J. Bourgeois, E. Montaudon and B. Maillard, *Can. J. Chem.*, 1991, **69**, 1320.
4 L. Vertommen, J. Meijer and B. Maillard, Akzo Chemicals, EP 89202889-5/1989.
5 H.-S. Dang and B. P. Roberts, *Tetrahedron Lett.*, 1992, **33**, 4621.
6 J. K. Kochi, in *Free Radicals*, ed. J. K. Kochi, Wiley Interscience, New York, 1973, vol. 2, pp. 665–710.
7 M. J. Bourgeois, B. Maillard and E. Montaudon, *Tetrahedron*, 1986, **42**, 5309.
8 J. March, in *Advanced Organic Chemistry*, Wiley Interscience, New York, 3rd edn., 1985, p. 901.
9 T. Nakata, K. Tokumaru and O. Simamura, *Tetrahedron Lett.*, 1967, 3303.
10 J. C. Scaiano, in *Oxygen Radicals in Biology and Medicine*, eds. M. G. Simic and K. A. Taylor, Plenum Publ., New York, 1989, p. 62.
11 C. Navarro, A. Saux, L. Vertommen and B. Maillard, *New J. Chem.*, 1992, **16**, 993.
12 C. Navarro, L. Vertommen and B. Maillard, *New J. Chem.*, 1992, **16**, 987.
13 J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 1965, **30**, 3272; J. K. Kochi, *J. Am. Chem. Soc.*, 1962, **84**, 1193.
14 A. Baignee, J. A. Howard, J. C. Scaiano and L. C. Stewart, *J. Am. Chem. Soc.*, 1983, **105**, 6120.
15 D. Avila, C. E. Brown, K. U. Ingold and J. Lusztyk, *J. Am. Chem. Soc.*, 1993, **115**, 466.
16 G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.
17 R. T. Sanderson, in *Chemical Bonds in Organic Compounds*, ed. S. Sand, Scottsdale AZ, 1976, p. 53.
18 E. R. Laird and W. L. Jorgensen, *J. Org. Chem.*, 1990, **55**, 9.
19 E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, 1956, **32**, 1381.
20 R. Criegee, *Ber. Dtsch. Chem. Ges.*, 1944, **77**, 722; R. Criegee, R. Kaspar, *Annalen der Chemie*, 1948, **560**, 127.
21 B. Giese, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 753.
22 A. Kharrat, G. Gardrat and B. Maillard, *Can. J. Chem.*, 1985, **63**, 2522.

---

* 1 Torr ≈ 133 Pa.

23 F. Ameer, S. E. Drewes, N. D. Emslie, P. T. Kaye, R. L. Mann, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2293.
24 J. Moulines, M. J. Bourgeois, M. Campagnole, A. M. Lamidey, B. Maillard and E. Montaudon, *Synth. Commun.*, 1990, **20**, 349.
25 W. Adam and A. Griesbeck, *Synthesis*, 1986, 1050.
26 E. Buncel and A. G. Davies, *Chem. Ind.*, 1956, 1052; E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1958, 1550.
27 R. F. Borch, *Tetrahedron Lett.*, 1972, **13**, 3761.
28 E. Montaudon, M. Agorrody, F. Rakotomanana and B. Maillard, *Bull. Soc. Chim. Belg.*, 1987, **96**, 769.

Paper 3/07331I
Received 13*th December* 1993
Accepted 22*nd December* 1993