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# Reaction of oxygen with γ,δ-ethylenic phenylhydrazones. Model reaction of end-group behavior in phenylhydrazine-accelerated oxidation of natural rubber

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**Summary** – An accurate definition of terminal groups of chains in the liquid polymers obtained by the phenylhydrazine-accelerated oxidation of natural rubber is needed. The object of the work was to use model molecules to explore the behavior of γ,δ-ethylenic methylketone phenylhydrazone end-groups in oxidation conditions. We have investigated the synthesis and characterization of models of these hypothetical end-groups, methylketones and phenones **1**, their phenylhydrazones **2**, the α-(phenyldiazenyl)hydroperoxides **3** resulting from reaction of **2** with oxygen, and the α-(phenyldiazenyl)alcohols **4** as characteristic derivatives of **3** or as models of possible reduced structures in oxidized liquid natural rubber. Three original syntheses of γ,δ-ethylenic ketones were carried out. In the case of γ,δ-ethylenic phenylhydrazones, the oxidation led to the expected α-(phenyldiazenyl)hydroperoxides and to epoxide derivatives of α-(phenyldiazenyl)alcohols **5** and ketones **6**. An intramolecular mechanism is proposed. The results are used to predict the possibilities of identification of the corresponding end-groups in liquid rubbers produced in this way.

**accelerated oxidation / natural rubber / phenylhydrazine / γ,δ-ethylenic ketone / γ,δ-ethylenic phenylhydrazone / α-(phenyldiazenyl)hydroperoxide / α-(phenyldiazenyl)alcohol / γ,δ-epoxyketone**

## Introduction

In the conversion of natural rubber to liquid natural rubber by phenylhydrazine/oxygen degradation, the acceleration of the oxidation process is explained by generation of phenyl radicals in the reaction of phenylhydrazine with oxygen. Our previous studies of this degradation process have allowed us to propose : (i) a chain-cleavage mechanism involving a phenyl radical addition and leading to oligomers with methylketone and phenone end-groups [1]; (ii) a consumption of methylketones by reaction with phenylhydrazine and conversion of phenylhydrazone to α-azohydroperoxide [1]; and (iii) a consumption of the oxidative system by a cyclic process involving the decomposition of α-(phenyldiazenyl)hydroperoxide (fig 1) [2].

In order to verify these hypotheses and precisely define the behavior of the end-groups during the oxidative process, we have considered the following as models for end-groups (fig 2) : (i) the γ,δ-ethylenic ketones **1a-e**, 6-methylhept-5-en-2-one **1a**, 6-methylnon-5-en-2-one **1b**, 5-methylnon-5-en-2-one **1c** (model of end-groups resulting from chain cleavage near a head-head diad), 5-methyl-1-phenyloct-4-en-1-one **1d** and 4-methyl-1-phenyloct-4-en-1-one **1e** (model of end-groups resulting from chain cleavage near a tail-tail diad), and the saturated ketones pentan-2-one **1f** and 1-phenylbutan-1-one **1g**; (ii) the γ,δ-ethylenic phenylhydrazones **2a-e** derived from **1a-e** and the saturated phenylhydrazones **2f** and **2g**; (iii) the γ,δ-ethylenic α-(phenyldiazenyl)hydroperoxides **3a-e** as expected **2a-e** oxidation products and the saturated α-(phenyldiazenyl)hydroperoxides **3f** and **3g**; and (iv) the corresponding α-(phenyldiazenyl)alcohols **4a-g**.

The methylketones **1a**, **1b** and **1f** and their corresponding phenylhydrazones **2a**, **2b** and **2f** have been considered previously as models of end-groups [1, 3]. We describe here the synthesis and characterization of the other model molecules.

The application of the Carroll reaction between vinylcarbinols and ketoesters (fig 3) was successful for the synthesis of **1b** (2-methylhex-1-en-3-ol and ethyl acetylacetate) [4] and has been considered for the synthesis of **1c** (2-methylhex-1-en-3-ol and ethyl acetylacetate), **1d** (2-methylhex-1-en-3-ol and ethyl benzoylacetate) and **1e** (3-methylhex-1-en-3-ol and ethyl benzoylacetate). The use of benzoylacetate in Carroll reactions has, to our knowledge, not yet been tested. Moreover, these syntheses allow us to follow the structural effects on the yields and stereospecificity of the Carroll reaction, which is known to induce the preferential formation of the *E* isomers [5].

* Correspondence and reprints

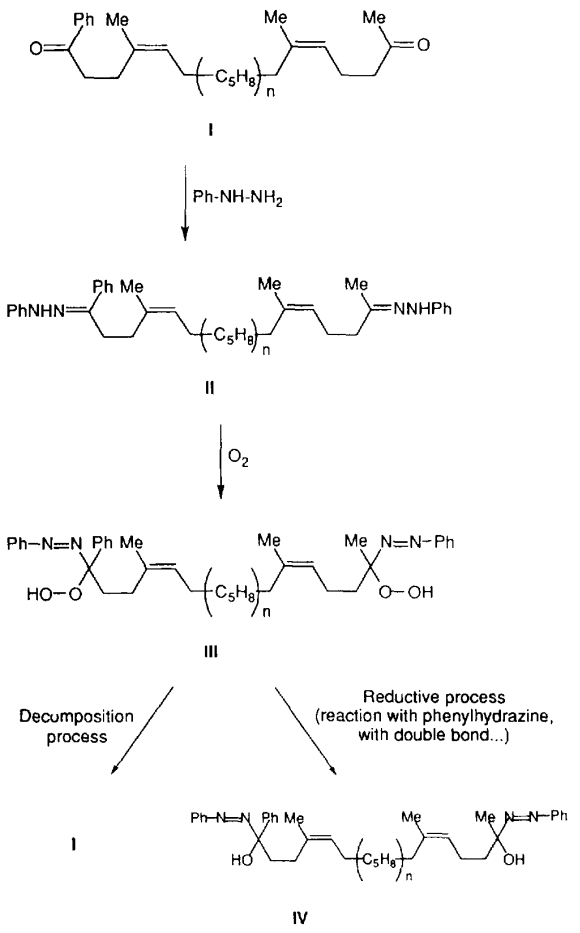
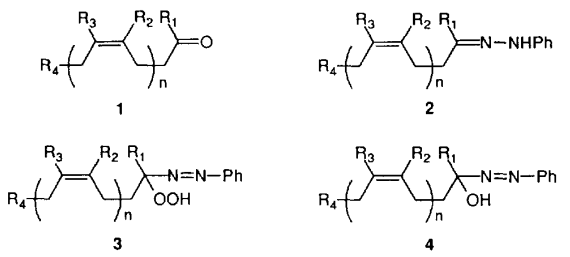



**Fig 1.** Hypothesis of end-group structures of oligomers from the degradation of natural rubber by the phenylhydrazine/oxygen system.

The phenylhydrazones **2a-g** were prepared by a standard process from the corresponding ketones. The phenylhydrazones are known to easily undergo autoxidation [6]. The simple reactions of **2a-g** with oxygen were therefore expected to lead to the $\alpha$-diazenylhydroperoxides **3a-g**. The experimental procedures were adjusted in order to minimize decomposition but secondary reactions are difficult to prevent. The selective reduction of **3a-g** by triphenylphosphine [7] was retained in order to obtain the corresponding $\alpha$-diazenylalcohols **4a-g**, whose identification was a further investigated proof of the formation of $\alpha$-diazenylhydroperoxides.

Secondary reactions have been investigated by the identification of the principal secondary products derived from **2a**. Global analysis of crude $\alpha$-diazenylhydroperoxides **3** and crude $\alpha$-diazenylalcohols **4** has provided a semi-quantitative evaluation of their proportions and those of the secondary products and/or structures. The results were explained by a general mechanism for oxidation of $\gamma,\delta$-ethylenic phenylhydrazones **2**.




| | 1a | 1b | 1c | 1d | 1e | 1f | 1g |
|---|---|---|---|---|---|---|---|
| | 2a | 2b | 2c | 2d | 2e | 2f | 2g |
| | 3a | 3b | 3c | 3d | 3e | 3f | 3g |
| | 4a | 4b | 4c | 4d | 4e | 4f | 4g |
| $n$ | 1 | 1 | 1 | 1 | 1 | 0 | 0 |
| $R_1$ | $CH_3$ | $CH_3$ | $CH_3$ | Ph | Ph | $CH_3$ | Ph |
| $R_2$ | H | H | $CH_3$ | $CH_3$ | H | | |
| $R_3$ | $CH_3$ | $CH_3$ | H | H | $CH_3$ | | |
| $R_4$ | H | $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | $C_2H_5$ |

**Fig 2.** Selected model molecules of liquid rubber end-groups : ketones **1**, phenylhydrazones **2**, expected $\alpha$-(phenyldiazenyl)hydroperoxides **3** by reaction of **2** with oxygen and expected $\alpha$-(phenyldiazenyl)alcohols **4** by reduction of **3**.

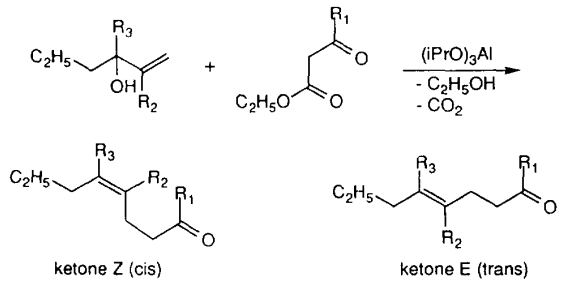


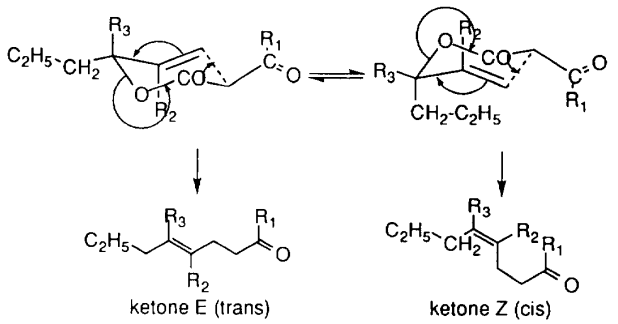

**Fig 3.** Synthesis of $\gamma,\delta$-ethylenic ketones **1b-e** by the Carroll reaction.

## Results and discussion

### *Synthesis and characterization of model molecules*

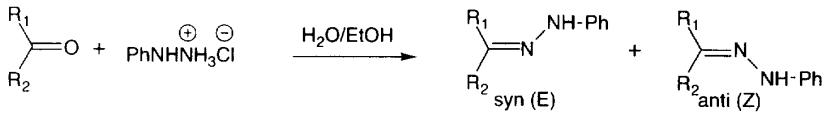
- *Ketones : Structural effects on yield and stereospecificity of the Carroll reactions*

The results of the Carroll reaction show that the yield is ketoester-dependent whereas its stereospecificity is vinylcarbinol-dependent. Indeed, the yields are higher with ethyl acetylacetate, which gives the expected $\gamma,\delta$-ethylenic methylketones **1b** (81%) and **1c** (80%), than with benzoylacetate, which gives the expected $\gamma,\delta$-ethylenic phenones **1d** (68%) and **1e** (69%). The $E/Z$ ratio is very much higher with isopropenylpropylcarbinol, which leads to the expected $\gamma$-methyl $\gamma,\delta$-ethylenic ketones **1c** (85:15) and **1d** (83:17), than with 3-methylhex-1-en-3-ol, which leads to the expected $\delta$-methyl $\gamma,\delta$-ethylenic ketones **1b** (57:43) and **1e** (54:46). The known stereospecificity of the Carroll reaction for preferential formation of the $E$-isomer has been verified. Considering the chair transition states (fig 4) in the concerted transfer mechanism operating on the




| | | Yield | | | |
|---|---|---|---|---|---|
| $R_1 = CH_3$ | **1b** | 81% | $R_3=CH_3$ | 57 | 43 |
| | **1c** | 80% | $R_3=H$ | 85 | 15 |
| $R_1 = Ph$ | **1d** | 68% | $R_3=H$ | 83 | 17 |
| | **1e** | 69% | $R_3=CH_3$ | 54 | 46 |

**Fig 4.** Concerted transfer mechanism in the Carroll reaction.




| | | | | |
|---|---|---|---|---|
| **1c** | $R_1$=Me, $R_2$=-$(CH_2)_2C(CH_3)$=CH(n-$C_3H_7$) | 79% | **2c** | 21% |
| **1d** | $R_1$=Ph, $R_2$=-$(CH_2)_2C(CH_3)$=CH(n-$C_3H_7$) | 79% | **2d** | 21% |
| **1e** | $R_1$=Ph, $R_2$= -$(CH_2)_2CH$=$CCH_3$(n-$C_3H_7$) | 53% | **2e** | 47% |

**Fig 5.** Synthesis of phenylhydrazones **2c-e** derived from $\gamma,\delta$-ethylenic ketones **1c-e**.

$\beta$-ketoester of the allylic alcohol formed by transesterification [5], the more effective stereospecificity in the Carroll reactions with isopropenylpropylcarbinol ($R_3$ = H) than with 3-methylhex-1-en-3-ol ($R_3$ = Me) can be explained by an increase of the predominance of the *E*-precursor conformer (conformer with propyl in the equatorial position) when the size of $R_3$ substituent decreases.

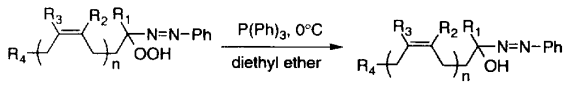
• *Synthesis of phenylhydrazones* : syn/anti *stereospecificity*

The phenylhydrazones **2c-e** derived from $\gamma,\delta$-ethylenic ketones **1c-e** were obtained in yields (fig 5) similar to those obtained in the syntheses of **2a**, **2b** and **2f** [3]. They were obtained as mixtures of stereomers with *cis/trans* geometry for double bond and *syn/anti* geometry for hydrazones. The *syn/anti* ratios were determined by $^1$H NMR from integration of the peak areas of $CH_3C$=N ($\delta$ = 1.75 [*syn*] and 1.95 ppm [*anti*] for methylketone phenylhydrazones and those of NH (peaks of unequal intensity at $\delta$ = 6.7 [*anti*] and 6.8 ppm [*syn*]) for phenone phenylhydrazones :

The conclusions of this analysis are supported by $^{13}$C NMR resolutions and correspond to the predominance of the more stable *syn* isomers.

• *Diazenylhydroperoxides and their corresponding α-diazenylalcohols : structural control of specificity*

The oxidation of phenylhydrazones into the corresponding $\alpha$-diazenylhydroperoxides (major products) was demonstrated by $^1$H NMR (table I) and $^{13}$C NMR (table II) analysis of the crude mixtures after reaction with oxygen and the stabilized mixtures obtained from the crude after reduction of hydroperoxides to hydroxides (fig 6).




3 4

**Fig 6.** Reduction of $\alpha$-diazenylhydroperoxides **3a-h** to $\alpha$-diazenylalcohols **4a-h** by $P(Ph)_3$.

However, there are unassigned signals in the NMR spectra and secondary products have been detected by HPLC. According to the known instability of $\alpha$-diazenylhydroperoxides [8], regeneration of the starting ketones with formation of phenol conforms with the spectroscopic and chromatographic anomalies for crude **3f** and **3g**, which come from saturated ketones. However it does not explain the results observed

**Table I.** $^1$H NMR of $\alpha$-diazenylhydroperoxides **3a-g** and their corresponding $\alpha$-diazenylalcohols **4a-g**.

| | $CH_3$ | $CH_2$ | $CH_2$ | $(CH_3)$ | CH | $CH_2$ | $CH_2$ | $CH_3$ | Z[3] |
|---|---|---|---|---|---|---|---|---|---|
| **3a**[1] | | | | 1.65 | 5.15 | 1.9-2.03 | 2.1-2.2 | 1.57 | 9.5 |
| | | | | 1.6 | $^3J$ = 7.1 | | $^3J$ = 7.8 | | |
| **4a**[1] | | | | 1.55 | 5.1 | 1.85-2 | 2.05-2.15 | 1.55 | 5.1 |
| | | | | 1.63 | $^3J$ = 7.1 | | $^3J$ = 7.7 | | |
| **3b**[1] | 0.8-0.95 | 1.32-1.45 | 1.85-1.95 | 1.63 *trans* | 5.1 | 1.95-2.05 | 2.13-2.23 | 1.56 | 9.75 |
| | | | $^3J$ = 7.5 | 1.73 *cis* | $^3J$ = 7.1 | | $^3J$ = 7.8 | | |
| **4b**[1] | 0.8-0.95 | 1.3-1.45 | 1.83-2 | 1.55 *cis* | 5.1 | 1.95-2.05 | 2.1-2.2 | 1.58 | 5.1 |
| | | | $^3J$ = 7.5 | 1.63 *trans* | $^3J$ = 7.1 | | $^3J$ = 7.7 | | |
| **3c**[1] | 0.8-0.95 | 1.25-1.4 | 1.9-2 | 1.6 *trans* | 5.15 | 2-2.13 | 2.13-2.23 | 1.58 | 9.55 |
| | | | | 1.7 *cis* | $^3J$ = 7.1 | $J$ = 7.6 | $^3J$ = 7.7 | | |
| **4c**[1,2] | 0.8-0.95 | 1.25-1.4 | 1.9-2 | 1.6 *trans* | 5.1 | 2-2.15 | 2.15-2.25 | | 5.1 |
| | | | | 1.7 *cis* | $^3J$ = 7.1 | $^3J$ = 7.6 | $^3J$ = 7.7 | | |
| **3d**[1,2] | 0.8-0.95 | 1.3-1.45 | 1.85-1.95 | 1.6 *trans* | 5.15 | 2.3-2.4 | 2.7-2.8 | | 9.75 |
| | | | | 1.7 *cis* | $^3J$ = 7.2 | $^3J$ = 7.7 | $^3J$ = 7.8 | | |
| **4d**[1,2] | 0.8-0.95 | 1.25-1.4 | 1.8-1.95 | 1.63 *trans* | 5.1 | 2.3-2.4 | 2.7-2.8 | | 5.6 |
| | | | | 1.7 *cis* | $^3J$ = 7.2 | $^3J$ = 7.7 | $^3J$ = 7.8 | | |
| **3e**[1,2] | 0.8-0.95 | 1.25-1.4 | 1.85-1.95 | 1.65 *trans* | 5.1 | 2.3-2.4 | 2.7-2.8 | | 9.75 |
| | | $^3J$ = 7.5 | 1.73 *cis* | $^3J$ = 7.2 | | $^3J$ = 7.5 | | | |
| **4e**[1,2] | 0.8-0.95 | 1.25-1.4 | 1.85-2 | 1.6 *trans* | 5.15 | 2.3-2.4 | 2.7-2.8 | | 5.65 |
| | | | $^3J$ = 7.5 | 1.7 *cis* | $^3J$ = 7.2 | | $^3J$ = 7.5 | | |
| **3f**[1] | 0.85-0.95 | 1.43-1.6 | | | | | 1.8-1.95 | 1.55 | 9.55 |
| **4f**[1] | 0.85-0.95 | 1.15-1.3 | | | | | 1.85-1.95 | 1.55 | 5.1 |
| | | 1.4-1.55 | | | | | $^3J$ = 7.8 | | |
| **3g**[1,2] | 0.85-0.95 | 1.35-1.5 | | | | | 2.05-2.15 | | 9.85 |
| | | | | | | | $^3J$ = 8.2 | | |
| **4g**[1,2] | 0.85-0.95 | 1.25-1.4 | | | | | 2.05-2.15 | | 5.55 |
| | | | | | | | 2.25-2.35 | | |

1) **Ph**-N=N : *ortho* = 7.4-7.5 ($^3J$ = 5.2); *para* = 7.4-7.5 ($^3J$ = 5.2); *meta* = 7.7-7.8 ppm ($^3J$ = 7.5)
2) **Ph**-C-(OOH) : *ortho* = 7.25-7.3 ($^3J$ = 6.7); *para* = 7.3-7.4 ($^3J$ = 7.5); *meta* = 7.6-7.7 ppm ($^3J$ = 8.2 Hz)
3) Z=OOH : **3a-g**; Z=OH : **4a-g**
$J$ in Hertz

for the crude **3a-e** which come from $\gamma,\delta$-ethylenic ketones. In these cases, we must bear in mind the ability of the $\alpha$-diazenylhydroperoxides to transfer oxygen atoms to alkenes [9], which would give epoxides **5** and/or **5'** (whose decomposition would give epoxyketones **6**) (fig 7), and the less foreseeable reactions of hydroxyl and phenyl radicals, which may occur during the decomposition [7d, 8, 10]. Moreover, considering the mechanism of phenylhydrazone oxidation [6b, 6c] and the possible cyclization of the ethylenic peroxy radical [11], the formation of epoxyketone structure **6** and/or cycloperoxidic structure **7** (fig 7) may be expected.

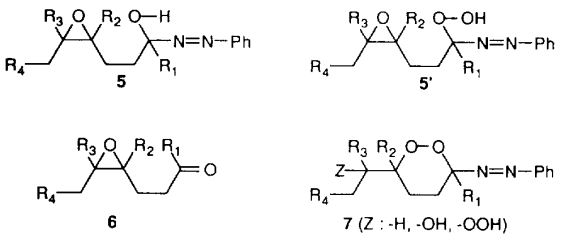



**Fig 7.** Hypothetical secondary oxidation products of $\gamma,\delta$-ethylenic phenylhydrazones **2a-f**.

Analysis of the NMR spectra supports the presence of epoxide structures ($^1$H NMR : $\delta$ = 1.25 and 1.3 ppm can be assigned to the methyl group of methyloxirane and $\delta$ = 2.7 ppm to the proton at the carbon of oxirane; $^{13}$C NMR : $\delta$ = 50-53 and 62-64 ppm can be assigned to carbons $C$-$CH_3$ and $C$-H of oxirane) and indicates the presence of cyclic peroxides ($^1$H NMR : $\delta$ = 4.2-4.4 ppm can be assigned to tertiary proton on cyclic peroxide; $^{13}$C NMR : $\delta$ = 82-84 ppm can be assigned to the carbons linked to oxygen in cyclic peroxide). Except for the variation resulting from the conversion of hydroperoxide to hydroxide, analysis of NMR spectra of the reduced **4a-g** have led to the same structural conclusions. The conversion of $\alpha$-diazenylhydroperoxides **3a-g** to $\alpha$-diazenylalcohols **4a-g** is not well observed in $^1$H NMR (table I) : Only the well-resolved hydrogen resonances of hydroperoxy ($\delta$ = 9.5 ppm) and hydroxy groups ($\delta$ = 5.2 ppm) seem to be significant. In contrast, the $^{13}$C NMR (table II) has very distinct characteristic signals for the hydroperoxy-linked quaternary carbon ($\delta$ = 105 ppm in **3a-h**) and the hydroxy-linked quaternary carbon ($\delta$ = 95 ppm in **4a-h**). In the same manner, chemical shifts of $\alpha$-$CH_2$ of $\alpha$-diazenylalcohols ($\delta$ = 39-40 ppm in **4a-h**) are at lower magnetic fields than those of $\alpha$-$CH_2$ of $\alpha$-diazenylhydroperoxides ($\delta$ = 35-36 ppm in **3a-h**) and chemical shifts of $\alpha$-$CH_3$ in $\alpha$-methyl $\alpha$-alcohols ($\delta$ = 24-26 ppm in **4a-c**) are at lower magnetic fields than those of $\alpha$-$CH_3$ in $\alpha$-methyl $\alpha$-alcohols ($\delta$ = 19-20 ppm in **3a-c**).

**Table II.** $^{13}C$ NMR of α-diazenylhydroperoxides **3a-g** and their corresponding α-diazenylalcohols **4a-g**.

| | $CH_3$ | $CH_2$ | $CH_2$ | $(CH_3)$ | C= | CH | $CH_2$ | $CH_2$ | $CH_3$ | C-Z[3] |
|---|---|---|---|---|---|---|---|---|---|---|
| **3a**[1] | | | | 17.7 | 132.3 | 123.6 | 21.9 | 35.6 | 19.5 | 105 |
| | | | | 25.7 | | | | | | |
| **4a**[1] | | | | 17.7 | 132.1 | 123.8 | 21.8 | 39.8 | 24.6 | 95.7 |
| | | | | 25.6 | | | | | | |
| **3b**[1] | 13.7 c | 21.1 c | 33.7 c | 15.75 c | 136.26 c | 124.2 c | 21.6 c | 35.6 c | 19.2 c | 105.18 c |
| | 13.67 t | 20.9 t | 41.7 t | 23.3 t | 136.06 t | 123.4 t | 21.75 t | 35.5 t | 19.2 t | 105.16 t |
| **4b**[1] | 13.67 c | 21 c | 33.7 c | 15.75 c | 135.6 c | 124.7 c | 21.5 c | 40.23 c | 25.8 c | 95.79 c |
| | 13.65 t | 20.9 t | 41.7 t | 23.3 t | 135.4 t | 123.8 t | 21.6 t | 40 t | 25.8 t | 95.81 t |
| **3c**[1] | 13.84 c | 23.1 c | 29.87 c | 23.3 c | 134.4 c | 125.3 c | 41.7 c | 34.05 c | 19.45 c | 105.1 c |
| | 13.81 t | 22.9 t | 29.92 t | 16.1 t | 134.3 t | 125 t | 33 t | 34.3 t | 19.45 t | 105.1 t |
| **4c**[1,2] | 13.85 c | 23.1 c | 29.87 c | 23.3 c | 134.6 c | 125.2 c | 41.7 c | 39.7 c | 25.6 c | 95.6 c |
| | 13.81 t | 22.9 t | 29.92 t | 16.1 t | 134.4 t | 125 t | 33 t | 39.6 t | 25.6 t | 95.6 t |
| **3d**[1,2] | 13.9 c | 23 c | 29.81 c | 23.3 c | 136.8 c | 125.3 c | 27 c | 34.2 c | | 106.5 c |
| | 13.8 t | 22.8 t | 29.88 t | 16.2 t | 136.8 t | 125.6 t | 33 t | 34.3 t | | 106.5 t |
| **4d**[1,2] | 13.8 c | 23 c | 29.81 c | 23.4 c | 136.7 c | 125.4 c | 27 c | 39.2 c | | 95.5 c |
| | 13.7 t | 22.8 t | 29.88 t | 16.2 t | 136.6 t | 125.6 t | 33 t | 39.3 t | | 95.5 t |
| **3e**[1,2] | 13.6 c | 21 c | 33.2 c | 15.7 c | 136.2 c | 123.3 c | 22.6 c | 34.4 c | | 105.8 c |
| | 13.5 t | 20.9 t | 41.5 t | 23.2 t | 136.3 t | 122.5 t | 22.8 t | 34.6 t | | 105.8 t |
| **4e**[1,2] | 13.8 c | 21 c | 33.2 c | 15.8 c | 136.3 c | 123.2 c | 22.4 c | 39.3 c | | 95.7 c |
| | 13.7 t | 20.9 t | 41.5 t | 23.4 t | 136.4 t | 122.6 t | 22.7 t | 39.2 t | | 95.7 t |
| **3f**[1] | 14.5 | 16.6 | | | | | | 37.9 | 19.5 | 105.2 |
| **4f**[1] | 14.4 | 16.3 | | | | | | 42.2 | 25.8 | 95.8 |
| **3g**[1,2] | 14.2 | 16.7 | | | | | | 41 | | 106.3 |
| **4g**[1,2] | 14.2 | 16.2 | | | | | | 44 | | 97.8 |

1) **3a-g** and **4a-g**; Ph(N=N) : C-*ortho* = 122.4-122.95; C-*para* = 128.7-129.3; C-*meta* = 131-131.7 ppm; C-(N=N)(OH) = 149.4-149.8; C-(N=N)(OOH) = 150.8-151.2
2) **3d, 3e, 3g** and **4d, 4e, 4g**; Ph(C-Z) : C-*ortho* = 126.8-127.2; C-*para* = 128.1-128.4; C-*meta* = 128.2-128.6 ppm; C-(OOH)(N=N) = 138.6-140; C-(OH)(N=N) = 139.7-142.6
3) Z=OOH : **3a-g**; Z=OH : **4a-g**
c : *cis*; t : *trans*

*Secondary structures and mechanisms*

The composition of the crude product derived from **2a** has been defined by the characterization of semi-preparative HPLC fractionated major product and HPLC identification of the minor products resolved by comparison with pure commercial or synthetic samples (fig 8).

The fractionation of the major product has confirmed its NMR identification as 1,5-dimethyl-1-(phenyldiazenyl)hex-4-enylhydroperoxide **3a**. The identification of the secondary product as 5,6-epoxy-6-methyl-2-(phenyldiazenyl)heptan-2-ol **5a** was improved by its HPLC resolution from **5'a** in mixtures obtained by conversion of residual double bond of crude **3a** in epoxide (fig 9). It was also identified by $^1H$ NMR as the major HPLC product in the crude mixture obtained by reduction of hydroperoxide of **5'a** in hydroxide according to the scheme.

$$\text{crude } \mathbf{3a} \xrightarrow{\text{monoperphthalic acid}} \mathbf{5'a} + \mathbf{5a} \xrightarrow{P(Ph)_3} \mathbf{5a}$$

The products corresponding to the minor HPLC peaks have been identified by comparison with biphenyl, phenol and 5,6-epoxy-6-methylheptan-2-one **6a**, juxtaposed in some cases with its bicyclic rearrangement product [12] **6'a** (fig 10). The identification of cycloperoxides **7a** requires their synthesis and was not carried out, but their presence would explain the unassigned HPLC peaks and cannot be eliminated.

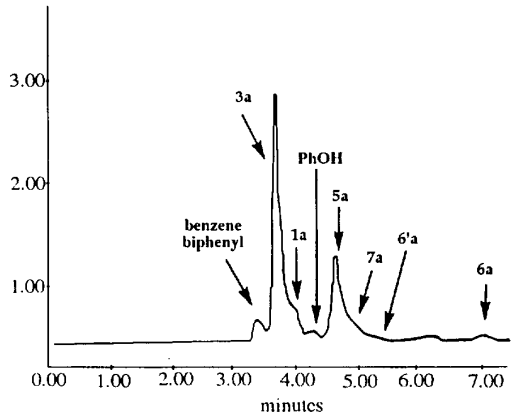



**Fig 8.** HPLC chromatogram of the crude mixture obtained from reaction of **2a** with oxygen (normal phase : Porasil column; solvent : $C_6H_{14}/CH_3COOEt$ : 70:30; D = 1 mL/min; UV detection : λ = 254 nm).

According to these results, the analogous **1b-e**, **5b-e**, **6b-e** and **6'b-e** must be considered as secondary components in the crude **3b-e**. The relative ratios of those constituents have been approached by a semi-quantitative analysis of $^1H$ NMR spectra (table III). The presence of ketones **1a-e** and/or **6a-e** is characterized by a δ = 2.3-2.4 ($-CH_2CO-$) signal for methyl-ketones and a δ = 2.7-2.8 ppm for phenones. The presence of epoxides **5a-e** and/or **6a-e** is characterized in

**Table III.** $^1$H NMR semi-quantitative evaluations of $\alpha$-azohydroperoxides **3** and secondary products in the crude oxidated mixtures.

| | **a** $R_1$=$CH_3$ $R_2$=H $R_3$=$CH_3$ | **b** $R_1$=$CH_3$ $R_2$=H $R_3$=$CH_3$ | **c** $R_1$=$CH_3$ $R_2$=$CH_3$ $R_3$=H | **d** $R_1$=Ph $R_2$=$CH_3$ $R_3$=H | **e** $R_1$=Ph $R_2$=H $R_3$=$CH_3$ | **f** $R_1$=$CH_3$ | **g** $R_1$=Ph |
|---|---|---|---|---|---|---|---|
| Azohydroperoxide **3** | 70% | 72% | 87% | 61% | 62% | 84% | 88% |
| Oxirane of **5** and/or **6** | ++ | ++ | | | + | | |
| Cycloperoxy of **7** and/or Dioxolane **6'** | + | traces | | | traces | | |
| Ketone in **1** or **6** | + | + | + | ++ | ++ | + | ++ |

++ : small amount present; + : very small amount present.

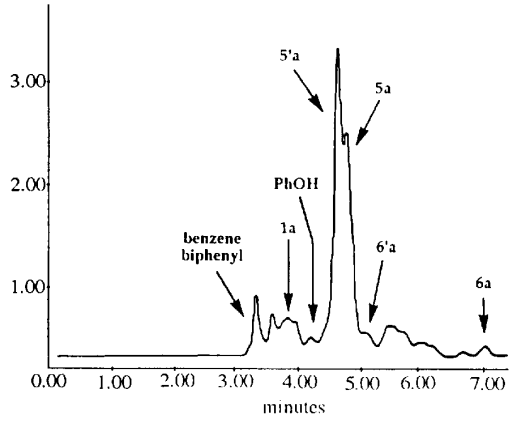



**Fig 9.** HPLC chromatogram of the epoxidation of crude **3a** by monoperphthalic acid (normal phase : Porasil column; solvent : $C_6H_{14}/CH_3COOEt$ : 70:30; D = 1 mL/min; UV detection : $\lambda$ = 254 nm).


**Fig 10.** Rearrangement of $\gamma,\delta$-epoxyketone **6a**.

the $^1$H NMR by a signal at $\delta$ = 2.5-2.9 ppm, well resolved from the (-$CH_2CO$-) signal in the derivatives of methylketones. Signals in the $\delta$ = 4.2-4.8 ppm zone could correspond to a cycloperoxy of **7** and/or to a bridge head proton of **6**.

It is noticeable that the secondary epoxy and cycloperoxy or bicyclic dioxolane derivatives are formed in higher proportions in the oxidations of **2a**, **2b** and **2e** than in those of **2c** and **2d**. The yields of the phenone diazenylhydroperoxides derivatives **3d** and **3e** were significantly lower than those of the corresponding methylketones derivatives.

To explain these results, we propose a general mechanism for oxidation of $\gamma,\delta$-ethylenic phenylhydrazones **2** (fig 11). According to the previously described mechanism [6b, 6c], the conversion of phenylhydrazones **2** to $\alpha$-diazenylhydroperoxides **3** involves the formation of the $\alpha$-(phenyldiazenyl)peroxy radical **A** and a transfer reaction. Because of the proximity, the intramolecular addition of **A** with the $\gamma,\delta$-double bond appears probable [11, 13], especially when the $\gamma$-C is substituent-free ($R_2$=H) as in the **a, b** and **e** series. This would lead to a cycloperoxy radical **B** that can (i) give rise to a transfer reaction and formation of **7** (Z=H); (ii) be decomposed in epoxidized alkoxy radical **C**; or (iii) react with oxygen to produce a cycloperoxy-peroxy radical **D**. Transfer reactions on **C** explain the formation of **5** and on **D** that of **7** (Z=OOH).

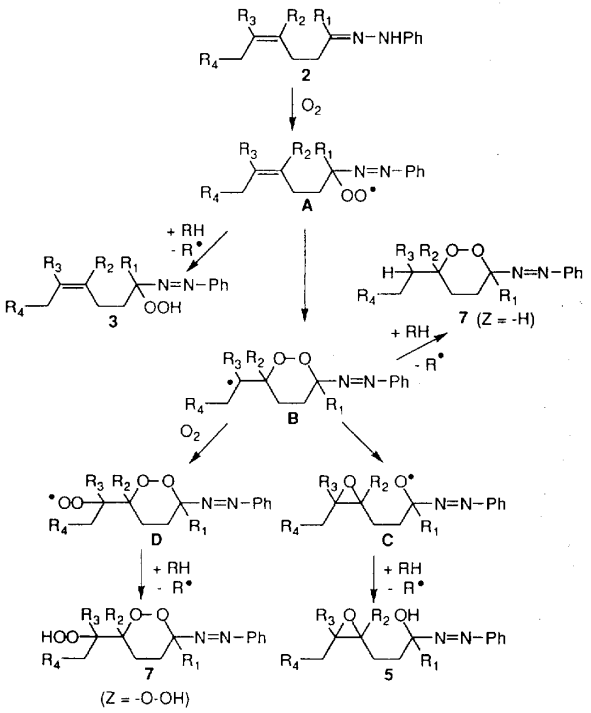



**Fig 11.** Plausible mechanism for the oxidation of $\gamma,\delta$-ethylenic phenylhydrazones.

The presence of **5** and/or **6**, and **7** and/or **6'** in the **a, b** and **e** series (indicated by the plus signs in table III) supports this mechanism, especially regarding the intramolecular epoxidation [13] which is clearly supported

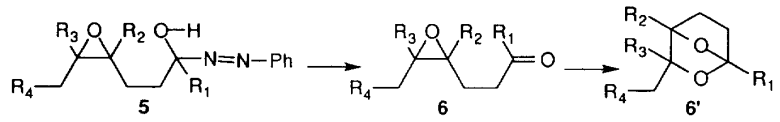
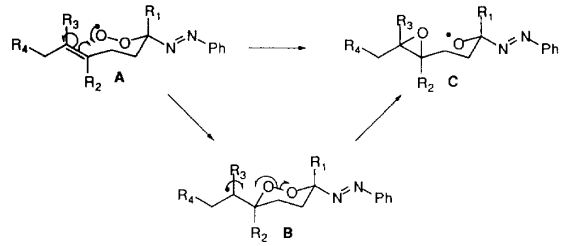


**Fig 12.** Formation of epoxidized ketones and bicyclic dioxolane by decomposition of epoxyazoalcohols.

by the identification of **5a**. This intramolecular epoxidation proceeds according to the same mechanism as the intermolecular epoxidation by peroxy radicals [14] :



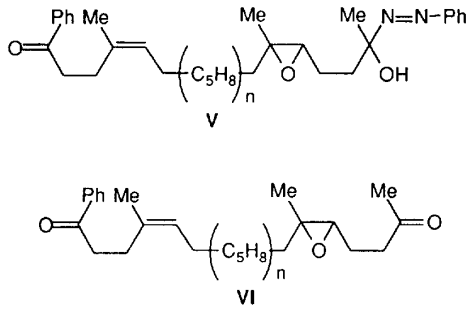
The instability of $\alpha$-diazenylhydroperoxides **3** explains the detection of ketonic structures, and phenol and biphenyl for the **a** series. The poor yields of $\alpha$-diazenylhydroperoxides **2d** and **2e** in the case of the phenone phenylhydrazone are the result of a higher instability of the $\alpha$-(phenyldiazenyl) $\alpha$-(phenyl)-hydroperoxides. The instability of $\alpha$-diazenylalcohols [9] explains the identification of **6a** in crude **3a** and leads us to consider the epoxyketones **6**, to explain some of the detected epoxy structures, and the rearranged bicyclic dioxolanes **6'** (fig 12), to explain the $\delta$ = 4-5 ppm $^1$H NMR resonances. The decomposition of cycloperoxidized **7**, especially when Z=OOH which probably induces C-C cleavage, must be considered in the general degradation process.

## Conclusion

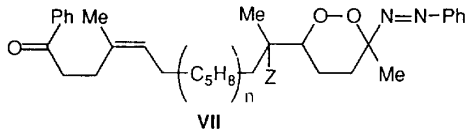
Our results confirm that if the expected methylketones are formed in the degradation of natural rubber by phenylhydrazine in the presence of oxygen then they are converted into phenylhydrazones, which react with oxygen to give the corresponding $\alpha$-diazenylhydroperoxides. The results on phenone model compounds lead us to propose that the presence of phenones in degradation mixtures from rubber model compounds could be the result of their regeneration by the preferred decomposition of the corresponding $\alpha$-diazenylhydroperoxides formed in the same way as those derived from methylketones.

The identification of secondary products or structures has allowed us to propose a general mechanism for the degradation process, which explains the formation of epoxyalcohols **5**, epoxyketones **6** and cyclic peroxides **7**.

The application of these results to liquid rubber suggests the possibility of accessing end-groups like **I**, **II** and **III**, such as the epoxidized $\alpha$-diazenyl $\alpha$-methyl alcohol chain-ends **V** and its decomposition product the epoxidized ketone **VI**.



The cycloperoxide **VII** is a transient structure responsible for the formation of $\gamma$,$\delta$-epoxidized structure.



Similar cycloperoxide groups have been characterized as primary oxidation structures in thermoxidized rubber [15] and identified as derivatives of polybutadienic and polyisoprenic hydroperoxide model compounds [13]. Considering their decomposition [15], they must be considered as issuing from a end-group degrafting oxidation process.

## Experimental section

*Measurements and materials*

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AC 400, at 400.13 and 100.62 MHz, respectively, in $CDCl_3$ with TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as liquid films. Some of the $^1$H NMR spectra (90 MHz) were recorded on a Varian FT 80A. UV/vis absorption spectra were recorded on a Varian DMS 100 spectrophotometer in EtOH. High performance liquid chromatography (HPLC) analysis were performed with a Waters apparatus equipped with a double detection UV and differential refractometry (Normal phase HPLC : Porasil column; solvent : $C_6H_{14}$/$CH_3COOEt$ : 70:30; D = 1 mL/min; UV detection : $\lambda$ = 254 nm; reverse-phase HPLC : $\mu$ Bondapack column; solvent : MeOH/$H_2O$ : 80:20; D = 1 mL/min; UV detection : $\lambda$ = 254 and 270 nm). Reverse-phase semi-preparative HPLC (C18 $\mu$ bondapack column; solvent : MeOH/$H_2O$ : 80:20; D = 2 mL/min). Gas chromatography analysis were performed on a Packard 438A (capillary column : $OV_1$ ; hydrogen as the carrier gas; temperature program : 60-300°C, 2.5°C/min). Microanalysis were carried out by the Laboratoire Central de microanalyses du CNRS (Lyon).

Chemicals and reagents were purchases from commercial sources at the highest level of purity available. Ethyl acetylacetate and butyraldehyde (Janssen) were purified by distillation. Commercial monoperphthalic acid (50 g) was extracted by diethyl ether (100 mL) and used in the so-obtained titrated ($I_2$-$Na_2S_2O_3/5H_2O$) solution.

The 3-methylhex-1-en-3-ol and 2-methylhex-1-en-3-ol (bp 106°C/0.35 mbar; $n_D^{23}$ = 1.431; $^1$H NMR (400.13 MHz, $CDCl_3$) : $\delta$ 0.85-1 (t, 3H, $CH_3CH_2$), 1.25-1.37 (m, 2H, $CH_3CH_2CH_2$), 1.45-1.55 (dt, 2H, $CH_3CH_2CH_2$), 1.73 (s, 3H, $H_3CC$=), 3.2 (s, 1H, O*H*), 4-4.2 (t, 1H, C*H*-C=), 4.8-5.05 (d, 2H, =$CH_2$) were obtained from the reaction of vinylmagnesium bromide with pentan-2-one and the reaction of isopropenylmagnesium bromide with butanal, respectively. The 6-methylhept-5-en-2-one **1a** is commercially available (normal phase HPLC : $R_t$ (min) : 3.94; reverse-phase HPLC : $R_t$ (min) : 2.15). The methylketone **1b** (normal phase HPLC : $R_t$ : 3.75; reverse-phase HPLC : $R_t$ : 2.90) and the phenylhydrazones **2a** (normal phase HPLC : $R_t$ : 3.63), **2b** (normal phase HPLC : $R_t$ : 3.55; reverse-phase HPLC : $R_t$ : 6.25 for the *syn* isomer and 6.63 for the *anti* isomer) and **2f** (normal phase HPLC : $R_t$ : 3.63; reverse-phase HPLC : $R_t$ : 2.56) were obtained as described previously [16].

*Synthesis of $\gamma,\delta$-ethylenic ketones*

An equimolar mixture of allylic alcohol (3-methylhex-1-en-3-ol or 2-methylhex-1-en-3-ol) and ketoester (ethyl acetylacetate or ethyl benzoylacetate) was heated in the presence of aluminum isopropoxide (1-3%) as a catalyst. When the theoretical amount of EtOH had distilled, the $\gamma,\delta$-ethylenic ketone **1b-e** was fractionated by distillation under reduced pressure. Resolution of the methyl groups in C=C $\alpha$ position in $^1$H NMR spectra, corresponding to *E* (1.6-1.7 ppm) and *Z* (1.7-1.75 ppm) isomers, allowed the evaluation of the *E*/*Z* proportions in $\gamma,\delta$-ethylenic ketones. In the case of the 6-methylnon-5-en-2-one **1a**, this attribution was confirmed by GC (gas chromatography).

• *6-Methylnon-5-en-2-one* **1b** *[4]*

Yield : 81%; bp 59.5-61°C/5.3 mbar; $n_D^{22}$ = 1.448. (Lit [4] : bp 113-114/0.07 mbar; $n_D^{20}$ = 1.444).

Normal phase HPLC : $R_t$ : 3.70 (UV) 3.75 min (RD); reverse-phase HPLC : $R_t$ : 2.68 (UV) 2.90 min (RD).

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.8-1 (3H, t, $CH_3CH_2$), 1.33-1.45 (2H, m, $CH_3CH_2$), 1.60 (s, 0.57 × 3H, $CH_3$-C= *E*-isomer), 1.67 (s, 0.43 × 3H, $CH_3$-C= *Z*-isomer), 1.85-1.95 (t, 0.57 × 2H, $^3J$ = 7.5 Hz, $CH_2C(CH_3)$= *E*-isomer), 1.95-2.05 (t, 0.43 × 2H, $^3J$ = 7.6 Hz, $CH_2C(CH_3)$= *Z*-isomer), 2.18-2.3 (t, 2H, =CHC$H_2$), 2.4-2.5 (t, 2H, $CH_2C$=O), 5.1 (t, 1H, $^3J$ = 7.1 Hz, =C-*H*). *E*/*Z* = $I_{1.60}/I_{1.67}$ = 57/43.

$^{13}$C NMR (100.62 MHz, $CDCl_3$), **1** *Z*-isomer : $\delta$ 13.8 ($CH_3CH_2$), 15.6 ($CH_3C$=), 21 ($CH_2CH_3$), 22.1 (=CH$CH_2$), 29.7 ($CH_3C$=O), 33.6 ($CH_2C$=), 43.8 ($CH_2C$=O), 123.2 (*C*H=), 136.4 (*C*=), 208.56 (*C*=O); **1** *E*-isomer : $\delta$ 13.6 ($CH_3CH_2$), 20.8 ($CH_2CH_3$), 22.3 (=CH$CH_2$), 23.2 ($CH_3C$=), 29.7 ($CH_3C$=O), 41.6 ($CH_2C$=), 43.6 ($CH_2C$=O), 122.5 (*C*H=), 136.2 (*C*=), 208.62 (*C*=O).

IR (film) : 1 718 (C=O), 1 671 (C=C), 1 411 ($CH_2C$=O), 1 359 $cm^{-1}$ ($CH_3C$=O).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L $mol^{-1}$ $cm^{-1}$) : 279 (41, n → $\pi^*$), 213 (1 110, $\pi \rightarrow \pi^*$).

• *5-Methylnon-5-en-2-one* **1c**

Yield : 80%; bp 70-71.5°C/8 mbar; $n_D^{22}$ = 1.445.

Normal phase HPLC : $R_t$ : 3.75 (UV) 3.78 min (RD); reverse-phase HPLC : $R_t$ : 2.78 (UV) 2.98 min (RD).

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.85-0.95 (t, 3H, $CH_3CH_2$), 1.27-1.4 (m, 2H, $CH_3CH_2$), 1.6 (s, 0.85 × 3H, $CH_3$-C= *E*-isomer), 1.67 (s, 0.17 × 3H, $CH_3$-C= *Z*-isomer), 1.9-2 (m, 2H, $CH_2CH$=), 2.15 (s, 3H, $CH_3C$=O), 2.23-2.3 (t, 2H, =$CCH_2$), 2.5-2.57 (t, 2H, $^3J$ = 7.7 Hz, $CH_2C$=O), 5.15 (t, 1H, $^3J$ = 7.1 Hz, =C-*H*). *E*/*Z* = $I_{1.60}/I_{1.67}$ = 85/15.

$^{13}$C NMR (100.62 MHz, $CDCl_3$), **1c** *Z*-isomer : $\delta$ : 13.34 ($CH_3CH_2$), 22.3 ($CH_2CH_3$), 22.95 ($CH_3C$=), 29.3 ($CH_3C$=O), 29.6 ($CH_2CH$=), 41.7 (=$CCH_2$), 41.9 ($CH_2C$=O), 125 (*C*H=), 134.5 (*C*=), 207.9 (*C*=O); **1c** *E*-isomer : $\delta$ 13.3 ($CH_3CH_2$), 15.5 ($CH_3C$=), 21.8 ($CH_2CH_2$), 29.3 ($CH_3C$=O), 29.5 ($CH_2CH$=), 33.2 (=$CCH_2$), 42 ($CH_2C$=O), 124.7 (*C*H=), 133.1 (*C*=), 208 (*C*=O).

IR (film) : 1 718 (C=O), 1 670 (C=C), 1 417 ($CH_2C$=O), 1 359 $cm^{-1}$ ($CH_3C$=O).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L $mol^{-1}$ $cm^{-1}$) : 275 (47, n → $\pi^*$), 214 (1 124, $\pi \rightarrow \pi^*$).

Anal calc for $C_{15}H_{18}O$ (154.25) : C, 77.87; H, 11.76; O, 10.38. Found : C, 78.03; H, 11.82; O, 10.50.

• *4-Methyl-1-phenyloct-4-en-1-one* **1d**

Yield : 68%; bp 126-127°C/1.3 mbar; $n_D^{22}$ = 1.523.

Normal phase HPLC : $R_t$ : 3.35 (UV) 3.49 min (RD); reverse-phase HPLC : $R_t$ : 5.52 (UV) 5.73 min (RD).

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.85-0.95 (t, 3H, $CH_3CH_2$), 1.25-1.4 (m, 2H, $CH_3CH_2$), 1.65 (s, 0.83 × 3H, $CH_3$-C= *E*-isomer), 1.73 (s, 0.17 × 3H, $CH_3$-C= *Z*-isomer), 1.93-2.03 (m, 2H, $CH_2CH$), 2.35-2.45 (t, 2H, =$CCH_2$), 3.1-3 (t, 2H, $^3J$ = 7.75 Hz, $CH_2C$=O), 5.2 (t, 1H, $^3J$ = 7.1 Hz, =C-*H*), 7.37-7.45 (t, 2H, $^3J$ = 7.6 Hz, *meta*), 7.45-7.55 (t, 1H, $^3J$ = 7.4 Hz, *para*), 7.9-8 (d, 2H, $^3J$ = 8.4 Hz, *ortho*). *E*/*Z* = $I_{1.65}/I_{1.73}$ = 83/17.

$^{13}$C NMR (100.62 MHz, $CDCl_3$), **1d** *Z*-isomer : $\delta$ : 13.9 ($CH_3CH_2$), 22.9 ($CH_2CH_3$), 23.3 ($CH_3C$=), 26.6 (=$CCH_2$), 30.05 ($CH_2CH$=), 37.5 ($CH_2C$=O), 125.9 (*C*H=), 128.3 (C Ar, *meta*), 128.5 (C Ar, *ortho*), 133 (C Ar, *para*), 136.9 (=*C*), 137.1 (*C* Ar), 199.9 (*C*=O); **1d** *E*-isomer : $\delta$ 13.8 ($CH_3CH_2$), 16.2 ($CH_3C$=), 22.9 ($CH_2CH_3$), 30.2 ($CH_2CH$=), 34.1 (=$CCH_2$), 37.55 ($CH_2C$=O), 125.3 (*C*H=), 128.1 (C Ar, *meta*), 128.6 (C Ar, *ortho*), 132.9 (C Ar, *para*), 136.9 (=*C*), 137.1 (*C* Ar), 200 (*C*=O).

IR (film) : 1 687 (C=O), 1 598, 1 581 (C=C Ar), 1 409 ($CH_2C$=O), 741, 692 $cm^{-1}$ (monosubstituted aromatic).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L $mol^{-1}$ $cm^{-1}$) : 278 (1110, n → $\pi^*$, C=O), 243, 203 (11 380 ($\pi \rightarrow \pi^*$), 20 620, Ph).

Anal calc for $C_{15}H_{20}O$ (216.32) : C, 83.29; H, 9.32; O, 7.40. Found : C, 83.01; H, 9.35; O, 7.31.

• *5-Methyl-1-phenyloct-4-en-1-one* **1e**

Yield : 69%; bp 136-138°C/1.3 mbar; $n_D^{23}$ = 1.516.

Normal phase HPLC : $R_t$ : 3.35 (UV) 3.41 min (RD); reverse-phase HPLC : $R_t$ : 5.74 (UV) 5.94 min (RD).

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.85-1 (t, 3H, $CH_3CH_2$), 1.3-1.45 (m, 2H, $CH_3CH_2$), 1.6 (s, 0.54 × 3H, $CH_3$-C= *E*-isomer), 1.67 (s, 0.46 × 3H, $CH_3$-C= *Z*-isomer), 1.9-2 (t, 0.54 × 2H, $^3J$ = 7.5 Hz, $CH_2C(CH_3)$= *E*-isomer), 2-2.1 (t, 0.46 × 2H, $^3J$ = 7.5 Hz, $CH_2C(CH_3)$= *Z*-isomer), 2.4-2.5 (t, 2H, =CHC$H_2$), 2.95-3.05 (t, 2H, $CH_2C$=O), 5.15 (t, 1H, $^3J$ = 7.2 Hz, =C-*H*), 7.4-7.5 (t, 2H, $^3J$ = 7.6 Hz, *meta*), 7.5-7.6 (t, 1H, $^3J$ = 7.3 Hz, *para*), 7.9-8 (d, 2H, $^3J$ = 8.6 Hz, *ortho*). *E*/*Z* = $I_{1.60}/I_{1.67}$ = 54/46.

$^{13}$C NMR (100.62 MHz, $CDCl_3$), **1e** *Z*-isomer : $\delta$ : 14 ($CH_3CH_2$), 15.8 ($CH_3C$=), 20.9 ($CH_2CH_3$), 22.8 (=CH$CH_2$), 33.8 ($CH_2C$=), 39 ($CH_2C$=O), 123.5

(*C*H=), 128.3 (C Ar, *meta*), 128.4 (C Ar, *ortho*), 133.2 (C Ar, *para*), 136.7 (=*C*), 136.9 (*C* Ar), 200.2 (*C*=O); **1e** *E*-isomer : $\delta$ 13.7 (*C*H$_3$CH$_2$), 21.1 (*C*H$_2$CH$_3$), 22.9 (=CH*C*H$_2$), 23.4 (*C*H$_3$C=), 38.8 (*C*H$_2$C=O), 41.8 (*C*H$_2$C=), 122.9 (*C*H=), 128.1 (C Ar, *meta*), 128.5 (C Ar, *ortho*), 132.92 (C Ar, *para*), 136.5 (=*C*), 137 (*C* Ar), 200.3 (*C*=O).

IR (film) : 1 685 (C=O), 1 598, 1 581 (C=C Ar), 1 410 (CH$_2$C=O), 743, 692 cm$^{-1}$ (aromatic monosubstituted).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L mol$^{-1}$ cm$^{-1}$) : 279 (1 270, n $\rightarrow \pi^*$, C=O), 242, 204 (14 900 ($\pi \rightarrow \pi^*$), 24 050, Ph).

Anal calc for $C_{15}H_{20}O$ (216.32) : C, 83.29; H, 9.32; O, 7.40. Found : C, 83.44, H, 9.32; O, 7.42.

• *5,6-Epoxy-6-methylheptan-2-one* **6a**

Careful managing of this synthesis is necessary to prevent the cyclization of the product into bicyclic dioxolane **6'a**. Epoxidation of magnetically stirred **1a** (10 mmol) methylene chloride (150 mL/aqueous 0.5 mol/L $NaHCO_3$ (30 mL) emulsion was performed at 0°C by dropwise adjunction of the adjusted amount of the titrated monoperphthalic acid diethylether solution for stoichiometry. Two hours after the end of the addition, the organic phase was washed successively with 0.1 mol/L NaOH (30 mL) and water and then dried on $Na_2SO_4$ before rapid evaporation and distillation.

Yield : 73%; bp 68-69°C/2.6 mbar (lit [12a] : bp 58-60°C/1.3 mbar).

Normal phase HPLC (RD) : $R_t$ : 7.03 (**6a**) and when **6'a** is present : 5.2 min.

$^1$H NMR (90 MHz, $CDCl_3$), $\delta$ : 1.26, 1.30 ($CH_3$ on oxirane), 1.75 (m, $CH_2$ on oxirane), 2.15 ($CH_3$-CO-), 2.5-2.9 (H on oxirane and $CH_2$-CO-). When **6'a** is present : 1.55 ($CH_3$ on bridge-head dioxolane), 4.23-4.40 (H on bridge-head dioxolane) with other unresolved resonances.

*Preparation of phenylhydrazones* **2a-g**

Phenylhydrazones **2a-g** were prepared by the standard process of condensation of phenylhydrazine hydrochloride with the appropriate carbonyl compound. Except for **2d** and **2e**, which were obtained as crude products, phenylhydrazones were distilled or recrystallized twice from methanol. All phenylhydrazones were stored under nitrogen.

• *5-Methylnon-5-en-2-one phenylhydrazone* **2c**

Yield : 81%; bp 163-165°C/4 mbar; $n_D^{23}$ = 1.548.

Normal phase HPLC (RD) : $R_t$ : 3.53 min; Reverse-phase HPLC (RD) : $R_t$ : 6.27 (*syn*) and 6.63 min (*anti*).

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.85-0.95 (t, 3H, C*H*$_3$CH$_2$), 1.27-1.4 (m, 2H, CH$_3$C*H*$_2$), 1.63 (s, 3H, C*H*$_3$-C= *trans-syn*), 1.65 (s, 3H, C*H*$_3$-C= *trans-anti*), 1.73 (s, 3H, C*H*$_3$-C= *cis-anti*), 1.75 (s, 3H, C*H*$_3$-C= *cis-syn*), 1.75 (s, 0.79 × 3H, CH$_3$-C=N, *syn*-isomer), 1.95 (s, 0.21 × 3H, CH$_3$-C=N, *anti*-isomer), 1.9-2 (m, 2H, C*H*$_2$CH=), 2.2-2.3 (t, 2H, =CC*H*$_2$), 2.35-2.45 (t, 2H, $^3J$ = 7.7 Hz, C*H*$_2$C=N), 5.15 (t, 1H, $^3J$ = 7.1 Hz, =C-*H*), 6.75-6.85 (NH and aromatic *p*-NH), 6.95-7.05 (aromatic *o*-NH), 7.15-7.25 (aromatic *m*-NH). $E/Z$ = $I_{1.63}/I_{1.7}$ = 79/21.

$^{13}$C NMR (100.62 MHz, $CDCl_3$), **2** *Z*-isomer : $\delta$ : 13.92 (*C*H$_3$CH$_2$), 14.38 (*C*H$_3$C=N), 16.1 (*C*H$_3$C=), 22.95 (*C*H$_2$CH$_3$), 29.9 (*C*H$_2$CH=), 34.7 (=*C*CH$_2$), 37.4 (*C*H$_2$C=N), 112.87 (C Ar, *ortho*), 119.43 (C Ar, *para*), 125.85 (*C*H=), 129.07 (C Ar, *meta*), 134.1 (*C*=), 146.1 (*C* Ar), 147.8 (*C*=N); **2** *E*-isomer : $\delta$ 13.78 (*C*H$_3$CH$_2$), 14.22 (*C*H$_3$C=N), 15.9 (*C*H$_3$C=), 23.11 (CH$_2$CH$_3$), 30.05 (*C*H$_2$CH=), 36.8 (=*C*CH$_2$), 37.7 (*C*H$_2$C=N), 112.93 (C Ar, *ortho*), 119.4 (C Ar, *para*), 125.1 (*C*H=), 129.1 (C Ar, *meta*), 134.2 (*C*=), 146 (*C* Ar), 146.5 (*C*=N).

IR (film) : 3 353 (NH), 1 662 (C=C), 1 602, 1 503 (C=C, Ar), 1 246 (C-N), 749, 693 cm$^{-1}$ (monosubstituted aromatic).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L mol$^{-1}$ cm$^{-1}$) : 273 (19 100), 206 (21 350).

• *4-Methyl-1-phenyloct-4-en-1-one phenylhydrazone* **2d**

Yield : 90% of a viscous crude product.

Normal phase HPLC (RD) : $R_t$ : 3.39 min; reverse-phase HPLC (RD) : $R_t$ : 6.06 min (unresolved *syn* and *anti* isomers).

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.83-0.95 (t, 3H, C*H*$_3$CH$_2$), 1.3-1.43 (m, 2H, CH$_3$C*H*$_2$), 1.68 (s, 3H, C*H*$_3$-C= *trans-syn*), 1.7 (s, 3H, C*H*$_3$-C= *trans-anti*), 1.75 (s, 3H, C*H*$_3$-C= *cis-anti*), 1.78 (s, 3H, C*H*$_3$-C= *cis-syn*), 1.93-2.05 (m, 2H, C*H*$_2$CH=), 2.25-2.3 (t, 2H, $^3J$ = 7.9 Hz, =CC*H*$_2$), 2.3-2.35 (t, 2H, $^3J$ = 7.9 Hz, =CC*H*$_2$), 2.65-2.73 (t, 2H, $^3J$ = 7.8 Hz, C*H*$_2$C=N), 2.73-2.8 (t, 2H, $^3J$ = 7.9 Hz, C*H*$_2$C=N), 5.25 (t, 1H, $^3J$ = 7.1 Hz, =C-*H*), 6.75-6.8 (t, NH, *anti*), 6.8-6.88 (t, NH, *syn*), 7.1-7.18 (d, 2H, $^3J$ = 7.7 Hz, aromatic *o*-NH), 7.2-7.28 (t, 2H, $^3J$ = 7.45 Hz, aromatic *m*-C=N), 7.2-7.28 (t, 1H, $^3J$ = 7.45 Hz, aromatic *p*-NH), 7.2-7.28 (t, 1H, $^3J$ = 7.45 Hz, aromatic *p*-C=N), 7.28-7.35 (t, 2H, $^3J$ = 7.6 Hz, aromatic *m*-NH), 7.73-7.8 (d, 2H, $^3J$ = 7.5 Hz, aromatic *o*-C=N). $E/Z$ = $I_{6.8-6.9}/I_{6.75-6.8}$ = 79/21.

$^{13}$C NMR (100.62 MHz, $CDCl_3$), **2d** *Z*-isomer : $\delta$ : 13.76 (*C*H$_3$CH$_2$), 22.76 (*C*H$_2$CH$_3$), 23.5 (*C*H$_3$C=), 29.8 (*C*H$_2$CH=), 34 (=*C*CH$_2$), 36.6 (*C*H$_2$C=N), 113.01 (aromatic *o*-NH), 120.06 (aromatic *p*-NH), 125.1 (aromatic *o*-C=N), 125.2 (*C*H=), 127.7 (aromatic *p*-C=N), 128.2 (aromatic *m*-C=N), 129.1 (aromatic *m*-NH), 134.12 (*C*=), 138.3 (C Ar $\alpha$-C=N), 144.7 (C Ar $\alpha$-NH), 145.25 (C=N); **2d** *E*-isomer : $\delta$ 13.7 (*C*H$_3$CH$_2$), 16.2 (*C*H$_3$C=), 22.66 (*C*H$_2$CH$_3$), 29.9 (*C*H$_2$CH=), 35.1 (=*C*CH$_2$), 37.3 (*C*H$_2$C=N), 113.06 (aromatic *o*-NH), 120.01 (aromatic *p*-NH), 125.31 (aromatic *o*-C=N), 125.97 (*C*H=), 127.66 (aromatic *p*-C=N), 128.15 (aromatic *m*-C=N), 129.02 (aromatic *m*-NH), 134.1 (*C*=), 138.4 (C Ar $\alpha$-C=N), 144.8 (C Ar $\alpha$-NH), 145.3 (*C*=N).

IR (film) : 3 340 (NH), 1 670 (C=C), 1 602, 1 504 (C=C, Ar), 1 253 (C-N), 749, 693 cm$^{-1}$ (monosubstituted aromatic).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L mol$^{-1}$ cm$^{-1}$) : 330,6 (12 000), 300 (9 500), 244 (10 700), 204 (25 100).

• *5-Methyl-1-phenyloct-4-en-1-one phenylhydrazone* **2e**

Yield : 90% of a viscous crude product.

Normal phase HPLC (RD) : $R_t$ : 3.38 min.

$^1$H NMR (400.13 MHz, $CDCl_3$), $\delta$ : 0.8-0.95 (t, 3H, C*H*$_3$CH$_2$), 1.3-1.45 (m, 2H, CH$_3$C*H*$_2$), 1.58 (s, 3H, C*H*$_3$-C= *trans-anti*), 1.62 (s, 3H, C*H*$_3$-C= *trans-syn*), 1.7 (s, 3H, C*H*$_3$-C= *cis-anti*), 1.72 (s, 3H, C*H*$_3$-C= *cis-syn*), 1.9-1.95 (t, 2H, $^3J$ = 7.5 Hz, C*H*$_2$C(CH$_3$)= *syn*), 1.95-2.05 (t, 2H, $^3J$ = 7.5 Hz, C*H*$_2$C(CH$_3$)= *anti*), 2.2-2.3 (t, 2H, =CHC*H*$_2$), 2.55-2.63 (t, 2H, $^3J$ = 7.7 Hz, C*H*$_2$C=N), 2.63-2.7 (t, 2H, $^3J$ = 7.7 Hz, C*H*$_2$C=N), 5.2 (t, 1H, $^3J$ = 7.1 Hz, =C-*H*), 6.75-6.8 (t, NH, *anti*), 6.8-6.88 (t, NH, *syn*), 7.1-7.18 (d, 2H, $^3J$ = 7.6 Hz, aromatic *o*-NH), 7.23-7.3 (t, 2H, $^3J$ = 7.4 Hz, aromatic *m*-C=N), 7.23-7.3 (t, 1H, $^3J$ = 7.4 Hz, aromatic *p*-NH), 7.23-7.3 (t, 1H, $^3J$ = 7.4 Hz, aromatic *p*-C=N), 7.3-7.38 (t, 2H, $^3J$ = 7.6 Hz, aromatic *m*-NH), 7.73-7.8 (d, 2H, $^3J$ = 7.5 Hz, aromatic *o*-C=N). $E/Z$ = $I_{6.8-6.9}/I_{6.73-6.8}$ = 67/33.

$^{13}C$ NMR (100.62 MHz, $CDCl_3$), **2e** *Z*-isomer : $\delta$ : 14 ($CH_3CH_2$), 15.9 ($CH_3C$=), 21.04 ($CH_2CH_3$), 24.2 (=$CCH_2$), 33.7 ($CH_2CH$=), 38.4 ($CH_2C$=N), 112.6 (aromatic *o*-NH), 119.3 (aromatic *p*-NH), 123.5 (CH=), 125.44 (aromatic *o*-C=N), 127.8 (aromatic *p*-C=N), 128.45 (aromatic *m*-C=N), 129.17 (aromatic *m*-NH), 135.6 (C=), 138.3 (C Ar $\alpha$-C=N), 144.6 (C Ar $\alpha$-NH), 147.09 (C=N); **2e** *E*-isomer : $\delta$ 13.7 ($CH_3CH_2$), 20.85 ($CH_2CH_3$), 23.3 ($CH_3C$=), 24.3 (=$CCH_2$), 38.2 ($CH_2C$=N), 41.7 ($CH_2CH$=), 113.1 (aromatic *o*-NH), 120 (aromatic *p*-NH), 122.5 (CH=), 125.5 (aromatic *o*-C=N), 127.77 (aromatic *p*-C=N), 128.26 (aromatic *m*-C=N), 129.06 (aromatic *m*-NH), 134.7 (C=), 137.6 (C Ar $\alpha$-C=N), 145.3 (C Ar $\alpha$-NH), 147.2 (C=N).

IR (film) : 3 340 (NH), 1 662 (C=C), 1 602, 1 504 (C=C, ar), 1 253 (C–N), 749, 691 $cm^{-1}$ (monosubstituted aromatic).

UV (EtOH) : $\lambda_{max}$ nm ($\varepsilon$ : L $mol^{-1}$ $cm^{-1}$) : 331 (11 100), 302.5 (9 400), 243.5 (9 800), 203.5 (24 400).

*Oxidation of phenylhydrazones and reduction of hydroperoxides : crude $\alpha$-(phenyldiazenyl)hydroperoxides and $\alpha$-(phenyldiazenyl)alcohols*

The $\alpha$-(phenyldiazenyl)hydroperoxides **3a-g** were easily prepared in high yields by oxidation of the phenylhydrazones with oxygen in benzene. The following description is typical. A mixture of phenylhydrazone derived from methylketone or phenone (7.65 mmol) in 40 mL benzene was magnetically stirred for 2 h while oxygen (0.4 L/min) was bubbled through the solution. The temperature of the reaction mixture was maintained at 10-15°C. The color of the solution changed from bright-yellow to orange. The evaporation of benzene under reduced pressure at 10°C gave the orange viscous crude liquid **3**. The $\alpha$-(phenyldiazenyl)hydroperoxides **3a-g** were reduced in diethylether at 0°C. A cold solution of diethylether containing a corresponding quantity of triphenylphosphine was added dropwise with stirring. After stirring for 1 h, the triphenylphosphine oxide was eliminated by filtration. The solution was evaporated under vacuum at 10°C to give an orange viscous liquid **4a-g**. All the $\alpha$-diazenylhydroperoxides and corresponding $\alpha$-diazenylalcohols were stored under nitrogen at −40°C.

IR of **3** : 3 640-3 200 $cm^{-1}$ with a maximum at 3 410 $cm^{-1}$ (hydroxyl stretching vibrations), 836 $cm^{-1}$ (O-O); 1 715 (weak, C=O) in crude **3a-c** and **3f** (methylketone) and 1 685 $cm^{-1}$ (broad, C=O) in crude **3d-e** and **3g** (phenone).

IR of **4** : similar to IR of **3** with disappearance of 836 $cm^{-1}$ (O-O).

• *Crude 1,5-dimethyl-1-(phenyldiazenyl)hex-4-enyl hydroperoxide* **3a**

Normal phase HPLC : $R_t$ (min) : 3.30 (minor biphenyl and/or benzene) 3.67 (major product : **3a**), 3.82 (minor phenol), 4.0 (minor product **1a**), 4.64 (first secondary product : **5a**), (4.8-5.2 – small shoulder to 4.64 – assignable to **7a** and or to **6′a**), 7.03 (minor product : **6a**).

HPLC (RD) for **4a** normal phase : $R_t$ : 3.60; reverse-phase : $R_t$ : 4.56 min.

$^1H$ NMR (400.13 MHz, $CDCl_3$) : according to the intensity of the secondary signals ($\delta$ = 2.3-2.4 of **1a**, $\delta$ = 2.5-2.6 of **5a** or **6a**, $\delta$ = 4.2-4.3 of **7a** or **6′a**), the relative intensities of the peaks assigned to **3a** (table I) in the oxidized crude product and **4a** in the reduced crude product are near 70 and 67%, respectively.

Reverse-phase semi-preparative HPLC has allowed the fractionation of **3a** ($R_t$ (min) : 13.2) from **5a** ($R_t$ (min) : 8.6) and other secondary products.

• *Crude 1,5-dimethyl-1-(phenyldiazenyl)oct-4-enyl hydroperoxide* **3b**

HPLC (RD) for **4b** : normal phase : $R_t$ : 3.46 min; reverse-phase : $R_t$ : 7.64 (*cis*) and 8.38 min (*trans*).

$^1H$ NMR (400.13 MHz, $CDCl_3$) : According to the intensity of the secondary signals ($\delta$ = 2.3-2.4 of **1b**, $\delta$ = 2.5-2.6 of **5b** or **6b**, $\delta$ = 4.2-4.3 of **7b** or **6′b**), the relative intensities of the peaks assigned to **3b** (table I) in the oxidized crude product and to **4b** in the reduced crude product are near 72 and 68%, respectively.

• *Crude 1,4-dimethyl-1-(phenyldiazenyl)oct-4-enyl hydroperoxide* **3c**

HPLC (RD) for **4c** : normal phase : $R_t$ : 3.46 min; reverse phase : $R_t$ : 7.67 (*cis*) and 8.41 min (*trans*).

$^1H$ NMR (400.13 MHz, $CDCl_3$) : according to the intensity of the secondary signals ($\delta$ = 2.5-2.6 of **1c**, and ArH of **2c**), the relative intensities of the peaks assigned to **3d** (table I) in the oxidized crude product and to **4c** in the reduced crude product are near 87 and 81%, respectively.

• *Crude 4-methyl-1-phenyl-1-(phenyldiazenyl)oct-4-enyl hydroperoxide* **3d**

HPLC (RD) for **4d** : normal phase : $R_t$ : 3.39 min; reverse-phase : $R_t$ : 7.4 min.

$^1H$ NMR (400.13 MHz, $CDCl_3$) : according to the intensity of the -$CH_2$-C(OOH)($CH_3$)-N=N- signal ($\delta$ = 2.7-2.8), the relative intensities of the peaks assigned to **3d** (table I) in the oxidized crude product and to **4d** in the reduced crude product are near 61 and 58% respectively.

• *Crude 5-methyl-1-phenyl-1-(phenyldiazenyl)oct-4-enyl hydroperoxide* **3e**

HPLC (RD) for **4e** : normal phase : $R_t$ : 3.38 min; reverse-phase : $R_t$ : 8.03 min.

$^1H$ NMR (400.13 MHz, $CDCl_3$) : according to the intensity of the -$CH_2$-C(OOH)($CH_3$)-N=N- signal ($\delta$ = 2.7-2.8), the relative intensities of the peaks assigned to **3e** (table I) in the oxidized crude product and to **4e** in the reduced crude product are near 62 and 59%, respectively.

• *Crude 1-methyl-1-(phenyldiazenyl)butyl hydroperoxide* **3f**

HPLC (RD) for **4f** : normal phase : $R_t$ : 3.64 min; reverse-phase : $R_t$ : 2.88 min.

$^1H$ NMR (400.13 MHz, $CDCl_3$) : according to the intensity of the -C(OO*H*)($CH_3$)-N=N- signal ($\delta$ = 2.7-2.8), the relative intensities of the peaks assigned to **3f** (table I) in the oxidized crude product and to **4f** in the reduced crude product are near 84 and 83%, respectively.

• *Crude 1-phenyl-1-(phenyldiazenyl)butyl hydroperoxide* **3g**

HPLC (RD) for **4g** : normal phase : $R_t$ : 3.61 min; reverse-phase : $R_t$ : 5.13 min.

$^1H$ NMR (400.13 MHz, $CDCl_3$) : according to the intensity of the -$CH_2$-C(OOH)($CH_3$)-N=N- signal ($\delta$ = 2.7-2.8), the relative intensities of the peaks assigned to **3g** (table I) in the oxidized crude product and to **4g** in the reduced crude product are near 88 and 84%, respectively.

• *Crude 5,6-epoxy-6-methyl-2-(phenyldiazenyl) heptan-2-ol* **5a**

Epoxidation of a magnetically stirred crude **3a** (4 mmol) diethylether (40 mL) solution was performed at 0°C by dropwise addition of a stoichiometrically adjusted amount

of the titrated monoperphthalic acid diethylether solution. Two hours after the end of the addition, the perphthalic acid was filtered. The solution containing the 5,6-epoxy-6-methyl-2-hydroperoxy-2-(phenyldiazenyl)heptane **5'a** was washed with $NaHCO_3$ and dried on $Na_2SO_4$. A fraction was taken for identification of crude **5'a**. The solution cooled to 0°C before the dropwise addition of triphenylphosphine (4 mmol) diethylether solution. One hour after the end of the addition, the triphenylphosphine oxide was filtered and the solution was evaporated to give the orange viscous crude **5a**.

Normal phase HPLC (RD) : sample before reduction with triphenylphosphine : $R_t$ (min) : 4.61 (**5'a**), 4.63 (**5a**) and the same signals of secondary products as in crude **3a**; crude final product : $R_t$ (min) : 4.65 (**5a**) and the same signals of secondary products as in crude **3a**.

$^1$H NMR (90 MHz, $CDCl_3$) : signals assigned to **5a**, $\delta$ : 1.26 (3H, $CH_3$ on oxirane ring), 1.30 (3H, $CH_3$ on oxirane ring), 2.75 (1H, t, $CH$ of oxirane ring), 1.6-1.8 (4H, m, $CH_2CH_2$), 1.55 (3H, s, $CH_3$-C(OH)-N=N-), 5.13 (1H, s, -O*H*), 7.46-7.70 (3H, *o,p*-ArH), 7.73-7.95 (2H, *m*-ArH).

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