Synthesis of α,β-Epoxyesters by Homolytically Induced Decomposition of Derivatives of Ethyl 2-(1-hydroperoxyethyl)propenoate

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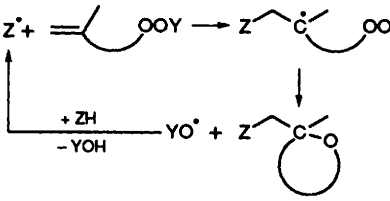
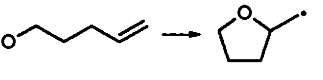
Decomposition of small amounts of *tert*-butyl peracetate at 110 °C in benzene solutions of derivatives of ethyl 2-(1-hydroperoxyethyl)propenoate afforded α,β-epoxyesters in good yields.

Synthetic applications of free-radical reactions have increased steadily throughout the last decade.[1] During this period we focused our attention on the study of homolytically induced decompositions of peroxy derivatives producing oxacyclanes[2] *via* a chain reaction [eqn. (1)].

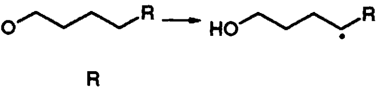
If the free-radical addition step occurred with high regioselectivity, the hydrogen abstraction by oxyl radicals from the substrate ZH, used as reaction solvent, produced in many cases several radicals.[2,3] A study of the induced decomposition of ethyl 2-*tert*-butylperoxymethylpropenoate in benzene[4] showed that formation of methyl radicals from *tert*-butoxyl radicals could be highly competitive with allylic hydrogen abstraction from the peroxide leading to ethyl 2-ethyl-2,3-epoxypropanoate in a yield of 40%. Such a result prompted us to investigate the use of the free-radical rearrangement of the oxyl radical YO·, produced in the S_Hi reaction, to generate the radical Z· involved in the addition reaction to the unsaturated peroxide. This communication presents preliminary results resulting from such a strategy.



(1)



(2)



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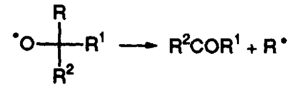
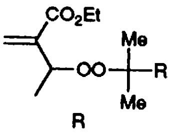
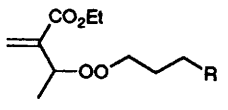


(4)

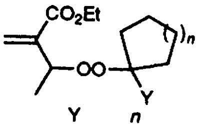
R^1 = alkyl or aryl, R^2 = alkyl or alkoxy group



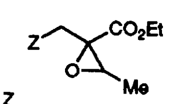
R
1 Me
2 OMe
3 Ph



R
4 Et
5 CH_2Ph
6 $CH{=}CH_2$

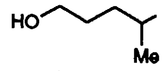


Y *n*
7 Me 1
8 OMe 0



Z
9 Me

10



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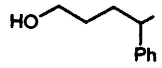

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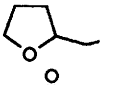

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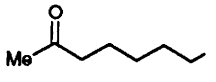

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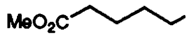

Several peroxidic derivatives were designed to generate oxyl radicals reacting *via* (*i*) intramolecular addition to a double bond [peroxide, eqn. (2)], (*ii*) intramolecular 1,5-hydrogen transfer [peroxide, eqn. (3)] or (*iii*) β-scission [peroxides and peroxyketals, eqn. (4)].

Peroxides **1** and **3–7** were easily prepared by the reaction of ethyl 2-bromomethylbut-2-enoate with the hydroperoxide;[5] peroxyketals **2** and **8** were respectively obtained in the condensation[6] of ethyl 2-(1-hydroperoxyethyl)propenoate[7] with 2-methoxypropene and 1-methoxycyclopentene under acidic catalysis (toluene-*p*-sulfonic acid).

Table 1 summarizes the results obtained in the induced decomposition of peroxy derivatives **1–8** in benzene. Standard conditions of reaction, previously employed to perform the induced decomposition of acrylic-type peroxydic compounds in various solvents,[2] were used in this study (benzene: **1–8**: *tert*-butyl peracetate molar ratio 20:1:0.1, 110 °C, 12 h).

The yields of formation of the various glycidic esters indicated that the strategy of using rearrangements of oxyl radicals to generate the radical Z• appears promising.

The lower yield observed for peroxide **5** was caused by the low efficiency of the benzylic radical in adding to the acrylic double bond as previously observed.[2] Allylic hydrogen abstraction by oxyl radicals could occur for all these peroxides[4] and particularly for **6**, decreasing the yield of epoxide.

Methyl radicals were produced from three different sources (*tert*-butoxyl, cumyloxyl or 1-methoxy-1-methylethoxyl radicals) with high efficiency. However, an easier synthesis of the peroxyketal (reaction of the hydroperoxide on a ketal or an enol ether) prompts us to recommend the use of such compounds as a general way to prepare substituted glycidic esters. Such an extension to various peroxyketals is under investigation at the moment.

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Table 1 Glycidic esters and peroxydic precursors

Peroxy derivative	Glycidic ester	Yield[a] (%)
1	**9**	67
2	**9**	82
3	**9**	90
4	**10**	83
5	**11**	40
6	**12**	53
7	**13**	60
8	**14**	88

[a] Isolated compound yields based on starting peroxy derivatives.

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