Table I. Room Temperature Magnetic Susceptibilities of Some $(\eta^5\text{-}C_5H_5)_2LnR$ Complexes[a]

Compound	Color	$10^6\chi_m$, cgs	μ_{eff}(obsd)	Theor[20]
Cp_2ErPh[b]	Pink	37,790	9.53	9.6
Cp_2GdPh	Lavender	24,408	7.69	7.94
Cp_2YbCH_3	Orange	7,225	4.14	4.5
Cp_2ErCH_3	Pink	37,985	9.41	9.6

[a] Measured by the Faraday method. [b] Cp = η^5-C_5H_5.

Table II. Variable Temperature Magnetic Susceptibilities

Compound	μ_{eff} (295°K)	μ_{eff} (195°K)	μ_{eff} (77°K)
$CpErCl_2 \cdot 3THF$[21]	9.68	9.68	
Cp_2HoCl[8]	10.30	10.30	
Cp_3Yb[22]	4.00	4.00	4.00
Cp_3Er[22]	9.45	9.44	9.45
Cp_2ErCH_3	9.41	9.37	8.95
Cp_2YbPh	3.86	3.75	3.43

ment with the theoretical values.[20] However, as the temperature was decreased, values of μ_{eff} were also found to decrease. This is in sharp contrast to other lanthanide–cyclopentadienyl compounds, where values for μ_{eff} do not vary with the temperature. Representative values for the different types of compounds (including the alkyls and aryls) are listed in Table II. This unusual reduction of μ_{eff} is tentatively attributed to enhanced quenching of the orbital angular momentum of the f electrons by the electric and/or ligand field of the R moiety. This would cause a reduction in the orbital moment and hence in μ_{eff}. This might be viewed as evidence for at least some degree of covalency in the σ bond.[23]

Clearly, these σ-bonded organolanthanide derivatives constitute an important new type of organolanthanide complex and, indeed, of organometallic compounds in general. Additional work is currently in progress in order to further elucidate the properties of these unusual new compounds.

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(24) Work done in partial requirement for the Ph.D. degree at TAMU.

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Free Radical Cyclization of Unsaturated Hydroperoxides

Sir:

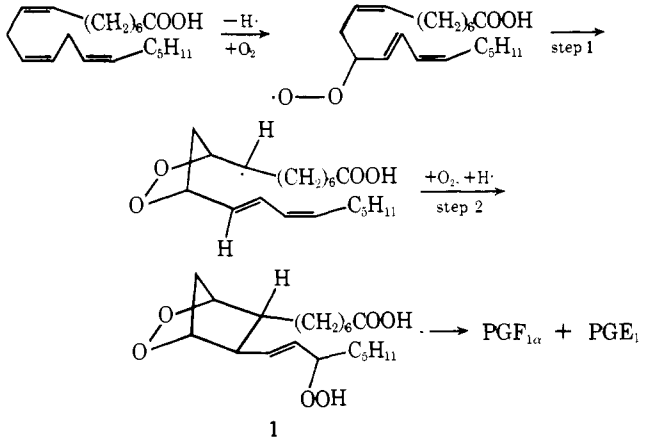
The biosynthesis of prostaglandins from polyunsaturated fatty acids has been studied by several investigators.[1] Although the precise details of the pathway of biosynthesis are unknown, the peroxy radical mechanism shown in Scheme I has been suggested.[2] In fact, an endo peroxide analogous to **1** has been isolated from the oxidation of arachidonic acid using the microsomal fraction of sheep vesicular gland as the enzyme source.[3]

Central to the proposed biosynthetic pathway are two consecutive radical cyclization reactions. In the first of these (step 1), the peroxide linkage is formed, while the second cyclization (step 2) completes the formation of the bicyclic peroxide structure.

In light of the potential importance of peroxy radical cyclizations in biological oxidation, it is remarkable that little information is available about this class of reaction. Peroxy radical cyclizations have been suggested[4] in the nonenzymic autoxidation of some unsaturated compounds, but the autoxidation format is not suitable for a systematic study of unsaturated peroxy radicals.

We report here a method for generating specific unsaturated peroxy radicals and also our preliminary observations regarding peroxy radical cyclizations. Of fundamental importance to this new method is the fact that hydroperoxide hydrogens (ROO*H*) are abstracted with relative ease by *tert*-butoxy radicals compared to the ease of abstraction of

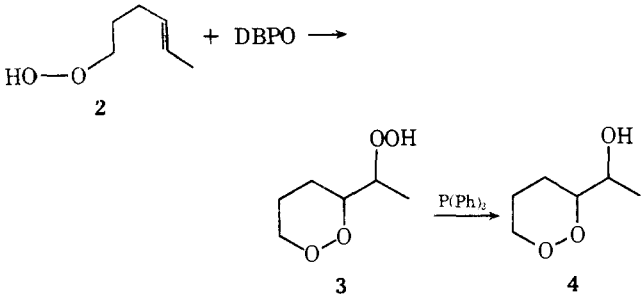
Scheme I



1

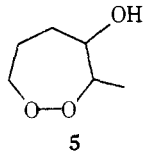
hydrogen attached to carbon. Thus the work of Howard and Ingold[5] and Walling[6] suggests that the relative rate of H atom abstraction by *tert*-butoxy radicals from ROO*H* compared to abstraction of an allyic H is approximately 50:1. The method reported here involves the formation of the requisite unsaturated peroxy radical by H atom transfer to *tert*-butoxy radicals from the corresponding hydroperoxide.

When the unsaturated hydroperoxide **2** (5.2 mmol)[7] is allowed to stand for 2 days with di-*tert*-butylperoxyoxalate (DBPO)[8] (2.0 mmol) in O_2 saturated benzene (500 ml) at 23° (four half-lives), a mixture of compounds is obtained which includes the two cyclic peroxides **3** and **4**. Although it



is possible to isolate these compounds directly by chromatography on silica gel it has been found more convenient to first reduce the hydroperoxide species in situ using triphenylphosphine (3.9 mmol). In this manner, the peroxy alcohol **4**, obtained analytically pure[9] as a mixture of threo and erythreo isomers, is isolated from the reduction reaction by silica gel chromatography in 30% overall yield.[10]

Although the NMR does not distinguish between the structure **4** and the corresponding seven-membered ring cyclization product **5**, double irradiation experiments show

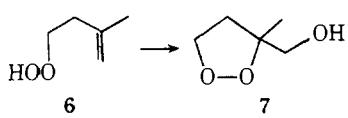


that the methyl group is clearly coupled to the proton α to the hydroxyl group suggesting **4** as the structure. Further confirmation of the structure assignment is provided by oxidation of the peroxy alcohol **4** with *N*-chlorosuccinimide, dimethyl sulfide[11] to a peroxy ketone which shows only a singlet in the α carbonyl region (2.28) of the NMR.

A mechanism consistent with our observations is presented in Scheme II.

According to this scheme, *tert*-butoxy radicals generated from DBPO homolysis abstract the hydroperoxy hydrogen yielding the peroxy radical. Cyclization and O_2 trapping leads ultimately to the peroxy hydroperoxide **3**.

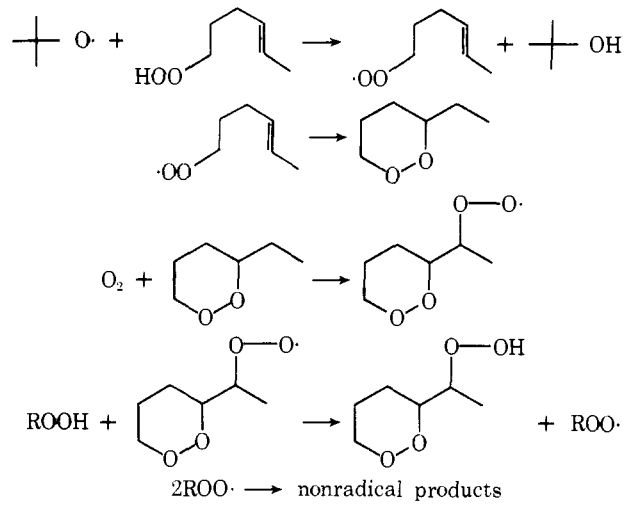
Treatment of hydroperoxide **6** with DBPO in benzene followed by triphenylphosphine reduction leads to the five-membered peroxy alcohol **7** in ≈25% overall yield. Peroxy



radicals thus appear to be subject to the same influences which cause carbon and alkoxy radicals to cyclize to five- rather than six-membered rings.[12]

The method reported here appears to be generally applicable to a systematic study of unsaturated peroxy radical cyclizations. In particular, model systems for radical cyclization leading to prostaglandin type products are currently under investigation in our laboratories.

Scheme II



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Application of Carbon-13 Magnetic Resonance to Isoprenoid Biosynthesis. I. Ovalicin

Sir:

The sesquiterpene ovalicin[1] (**1**) isolated from culture filtrates of the fungus *Pseudorotium ovalis* STOLK, shows antibiotic as well as immunosuppressive and antitumor ac-