Supporting Information

Calculations

Table S1. Experimental and Theoretical Spin Density Distribution in (*E,E*)-1,4-Pentadien-3-yl Radicals.

Method	(*E,E*)-1,4-Pentadien-3-yl			*Z,Z*-(*E,E*)-2,5-Heptadien-4-yl		
	$S_{C1,C5}$	S_{C3}	**$S_{C3}/S_{C1,C5}$**	$S_{C2,C6}$	S_{C4}	**$S_{C4}/S_{C2,C6}$**
RHF/6-31G*[a]	0.941	0.952	**1.01**	0.924	0.961	**1.04**
MP2(full)/6-31G*[a]	0.897	0.957	**1.07**	0.877	0.967	**1.10**
QCISD(T)/6-311G**// MP2(full)/6-31G*[a]	0.898	0.940	**1.05**	0.890	0.945	**1.08**
B3LYP/6-31G*	0.513	0.549	**1.07**	0.545	0.488	**1.12**
B3LYP/EPR-II	0.485	0.505	**1.04**	0.465	0.502	**1.08**
Experiment[b]	0.357	0.414	**1.16**	*c*	*c*	**<1.26[c]**

[a]From G2MP2 calculation of bis-allylic C-H BDE; 77.3 kcal/mol for 1,4-pentadiene and 76.8 kcal/mol for Z,Z-2,5-heptadiene. [b]Spin densities obtained from the experimentally determined α-hfcc s. [c]Not determined, but $S_{C2,C6} = 0.352$, $S_{C4} = 0.425$ yielding $S_{C4}/S_{C2,C6} = 1.21$ in *E*-2,5-hexadien-4-yl allows us to estimate a value of <1.26.

The (*E,E*)-1,4-pentadien-3-yl radical has a minimum energy structure of C_{2v} symmetry and has a $^2B_1$ electronic state. It is interesting to note that when studying the *Z,Z*-(*E,E*)-2,5-heptadien-4-yl radical, when the geometry is forced to be of C_{2v} symmetry (and the corresponding $^2B_1$ state), there is an imaginary vibrational mode corresponding to low barrier rotations of the terminal methyl groups. Breaking symmetry (giving a C_1 structure) and optimizing the geometry of the radical with tighter convergence criteria leads to a structure with all positive vibrational modes, and an electronic energy of —0.3 kcal/mol by UHF/6-31G(d), and —0.9 by ROB3LYP/6-311G(2d,2p) at the HF minimum energy geometry.

The autoxidation of 1,4-cyclohexadiene yields products consistent with 40% of oxygen addition to form a bis-allylic peroxyl radical, whereas 60% of oxygen addition occurs at either of the terminal positions of the pentadienyl system in the cyclohexadienyl radical.[1] This translates to a 1:1.33:1 relative spin distribution on the first, third and fifth carbon of the radical. Interestingly, theoretical calculations (B3LYP/6-31G*) yield the same spin density distribution in the C_{2v} ($^2B_1$) cyclohexadienyl radical (1:1.32:1).[2]

It is of interest to note that spin densities predicted by theory (Table 1) do not accurately reflect the product ratios seen in the competition experiments described here, i.e., 1:1.08:1 (B3LYP/6-31G*) versus 1:1.45-1.51:1 (experiment). The ratios of the spin densities are in reasonable agreement with experimental ESR measurements (which also predict a lower relative amount of addition at the central carbon atom), and there is good agreement between the G2MP2-calculated central C-H BDE in the pentadienylic systems and experimental values. We also note that theory predicts more spin on the central carbon atom of the cyclohexadienyl radical relative to that in the acyclic pentadienyl radical.

[1] Pan, X.-M.; Schuchmann, M. N.; von Sonntag, C. *J. Chem. Soc. Perkin Trans. 2* **1993**, 1021-1028.
[2] Kranenburg, M.; Ciriano, M. V.; Cherkasov, A.; Mulder, P. *J. Phys. Chem. A* **2000**, *104*, 915-921. This has also been confirmed by us.

The difference in rates of β-fragmentation of the 9/13-peroxyl and the 11-peroxyl are best understood in terms of the calculated[3] C-OO• bond dissociation enthalpy (BDE) of each of the two peroxyl radicals. The terminal peroxyls (9/13) have a much stronger C-OO• BDE (9.9 kcal/mol), leading to a lower rate of β-fragmentation (430 s^{-1}), whereas the bis-allylic peroxyl (11) has a much weaker C-OO• BDE (**3.6** kcal/mol), leading to a much higher rate of β-fragmentation (1.9 x 10^6 s^{-1}). The difference in the calculated BDE s (**6.3** kcal/mol) compare very well with experiment, as the ratio of the rate constants allow us to derive $\Delta E_a = 6.6$ kcal/mol from the ratios of the Arrhenius functions, assuming an A-factor of 1 log unit larger in the case of the dissociation of the bis-allylic peroxyl since an extra rotation must become frozen in the transition state for C-OO• dissociation.

Determination of k_{inh}

At low concentrations of any inhibitor, Eq. 1 reduces to Eq. 2, for which α and $k\beta$ have been determined. Thus, $\alpha = 0.43 -0.02$ and $k_\beta = 1.9 (-0.2)$ x 10^6 s^{-1}.

$$\frac{[4]}{[3 + 5]} = \frac{k_{inh}\,[\text{Inhibitor}]}{k_\beta} \bullet \frac{\alpha}{1 - \alpha} \qquad \text{Eq. 2}$$

Plotting [**4**]/[**3+5**] vs. inhibitor concentration gives a line with slope defined by Eq. 2, the only unknown being k_{inh}.

HPLC Standardization

Figure S1. HPLC standardization. Detection at 207 nm, NMR standardized by integration of 1 vinylic hydrogen from 3 and 5 (dd, 6.5δ) and two vinylic hydrogens from 4 **(t, 5.35δ).**

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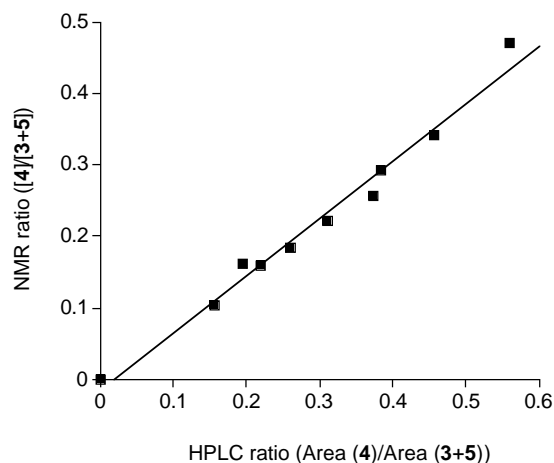
[3] ROB3LYP/6-311+G(2d,2p)//UHF/6-31G(d)-calculated BDE s are for *cis*,*trans*-2-peroxyl-3,5-heptadiene (model of 9/13-MeLinOO•) and *cis*,*cis*-4-peroxyl-2,5-heptadiene (model of 11-MeLinOO•).

Data for Figure 1

Table S2. Values of [4]/([3]+[5]) Determined *vs.* [α-tocopherol][a]

[toc] (M)	[4]/[3+5]	[4]/[3+5]	[4]/[3+5]	[4]/[3+5]	Average	Std dev.
1.76	0.551	0.577	0.602	0.534	0.566	0.030
1.54	0.601	0.566	0.542	0.535	0.561	0.030
1.32	0.554	0.557	0.577	0.528	0.554	0.020
1.10	0.536	0.546	0.528	0.505	0.529	0.017
0.88	0.481	0.494	0.481	0.491	0.487	0.007
0.79	0.474	0.466			0.470	0.006
0.69	0.421	0.441			0.431	0.014
0.50	0.348	0.393			0.371	0.032
0.30	0.248	0.277			0.263	0.021
0.10	0.107	0.122			0.115	0.011
0.72	0.456	0.455			0.456	0.001
0.62	0.434	0.418			0.426	0.011
0.52	0.394	0.386			0.390	0.006
0.41	0.343	0.344			0.344	0.001
0.21	0.210	0.190			0.200	0.014
0.10	0.113	0.108	0.119	0.106	0.112	0.006
0.08	0.088	0.088	0.082	0.088	0.087	0.003
0.05	0.060	0.062	0.060	0.060	0.061	0.001
0.03	0.033	0.033	0.035	0.033	0.034	0.001
0.01	0.017	0.017			0.017	0.000
0.03	0.040	0.042			0.041	0.001
0.02	0.025	0.025			0.025	0.000
0.02	0.020	0.021			0.021	0.001
0.01	0.020	0.019			0.020	0.001

a. Each value of [4]/[3]+[5] represents an independent experiment at the given concentration of [α-tocopherol]

Figure S2. HPLC/MS of Oxidation Mixture of Cholesterol Linoleate. Silver ion Complexes Observed by Selected Ion Monitoring (SIM) and Selected Reaction Monitoring (SRM). See reference 7 for details of chromatography and MS.