in Py on going from SDS to the smaller SDeS. These trends are explainable: the more polar HC derivatives and their corresponding CT complexes with MV^{2+} should prefer more polar solubilization sites. The SDS/SDeS and butadiene/stilbene differences can both be attributed to size effects. A reasonable estimate of the "length" of stilbene in terms of effective CH_2 groups is ca. 10,[22] and *trans,trans*-1,4-diphenyl-1,3-butadiene is certainly "longer" such that the two rigid molecules are comparable in length to the micelle radius in any reasonable model for the surfactant aggregate; clearly then the HC–MV^{2+} complexes are of significant size or volume compared to the SDS or SDeS aggregates that solubilize them. Obviously the probability of the hydrocarbon portion of the aggregate completely "swallowing" the CT complexes decreases as the size of the complex increases, or the length of the detergent chain decreases, and it is thus more likely that greater exposure to the aqueous phase will result. It is probably not necessary or prudent to speculate further on the nature of the various solubilization sites other than to suggest that they are probably moderately polar and, hence, "interfacial". What is noteworthy about the results obtained is the pronounced difference in solubilization sites for such small variations in complex and detergent structure. This underlines the danger of ascribing a single "character" to the solvent environment provided by detergent micelles and helps to reconcile apparent contradictions raised by different studies employing different techniques or probes to assess the solvent properties of aqueous surfactants.

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EPR Spectra of Some α-Tocopherol Model Compounds. Polar and Conformational Effects and Their Relation to Antioxidant Activities[1]

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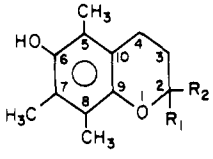
We recently reported[3,4] absolute rate constants, k_1, for the reaction of α-tocopherol (**1a**) and some related phenols (ArOH)



1a $R_1 = CH_3$, $R_2 = C_{16}H_{33}$

1b $R_1 = CH_3$, $R_2 = CH_3$

1c $R_1 = CH_3$, $R_2 = CO_2H$

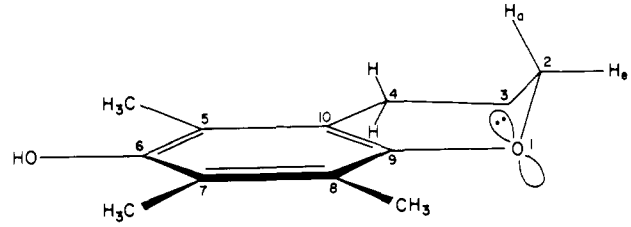
1d $R_1 = CH_3$, $R_2 = CO_2CH_3$

1e $R_1 = H$, $R_2 = H$

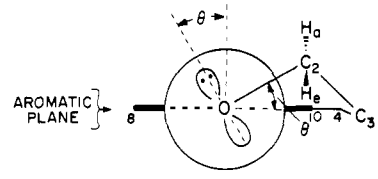
with poly(peroxystyryl)peroxyl radicals (ROO·) at 30 °C (eq 1).

$$ROO\cdot + ArOH \xrightarrow{k_1} ROOH + ArO\cdot \quad (1)$$

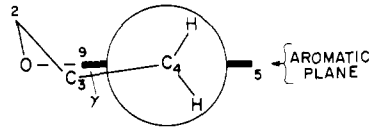
Compounds **1a** and **1b** were found to be more reactive toward ROO· than any other phenolic, chain-breaking antioxidants (k_1(**1a**) = 3.2 × 10^6, k_1(**1b**) = 3.8 × 10^6 M^{-1} s^{-1}).[4] This was attributed to stereoelectronic factors relating to the orientation of the p-type lone pair on the oxygen in position 1 with respect to the aromatic ring. This lone pair will stabilize the phenoxyl radical—and hence make the phenol a better antioxidant—provided its orbital can overlap with the orbital containing the unpaired electron. The extent of the stabilization is expected to follow a $\cos^2\theta$ relation, where θ is the dihedral angle between the O_1–C_2 bond and the C_8–C_9–C_{10} plane. By inference θ is also the dihedral angle between the 1-oxygen's p-type lone-pair orbital and the p-orbital of the adjacent aromatic carbon (see **2a** and **2b**).



2a



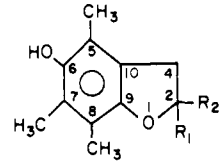
2b



2c

Maximum stabilization will occur when $\theta = 0°$. The fused-ring system in **1a** ensures that θ will at least tend to approach this value, and indeed, an X-ray structure for **1b**[3] gives $\theta = 18.5°$ and $15.2°$.[5,6] In contrast, k_1, for the ring-opened analogue, 4-methoxy-2,3,5,6-tetramethylphenol, is only 2.1 × 10^5 M^{-1} s^{-1}.[3] This compound has $\theta = 90°$ so that stabilization is minimized.

Work aimed at gaining additional understanding of the factors that control k_1 led to the discovery of a compound, **3a**, that was



3a $R_1 = CH_3$, $R_2 = H$

3b $R_1 = CH_3$, $R_2 = CO_2H$

1.66 times as reactive toward ROO· as **1a** and 1.43 times as reactive as **1b**.[4] Although some enhanced activity was anticipated because of the expected decrease in θ, the magnitude of the enhancement was surprising. That is, if in **1b** θ has the average value of 16.85°, then even if θ is 0° in **3a** the increase in the extent of stabilization would be only 1.09 (=$1/\cos^2 16.85°$). The increase

(1) Issued as NRCC No. 22670.
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(5) There are two different molecules in the unit cell.
(6) These angles differ slightly from those given originally,[3] which corresponded to the dihedral angle between the C_8–C_9 bond and the O_1–C_2 bond.

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Table I. EPR Spectral Parameters for Some Phenoxyl Radicals Related to α-Tocopheroxyl[a]

parent phenol	g	a^H, G 2	4(CH_2)	5(CH_3)	7(CH_3)	8(CH_3)	ref
1a			1.47	5.98	4.57	0.94	8
1b			1.46	5.94	4.51	0.96	8
1b	2.004 76		1.48	6.04	4.55	0.96	this work
1d	2.004 75		1.55	6.35	4.72	1.06	this work
1e	2.004 75	3.30 (1 H)[b]	1.41	6.02	4.64	1.00	this work
3a	2.004 68	1.98 (1 H)	0.28	5.80	4.75	1.10	this work
3b	2.004 62		[c]	6.00	4.95	1.11	this work

[a] For experimental conditions, see text. The numbering schemes are shown in 1 and 3. Note that in 3 the position 3 is a "phantom" position so as to simplify comparison of the H hfs's on the aromatic ring. Our hfs's were obtained by computer simulation and are reliable to ±0.03 G. [b] Second H not resolved, $\Delta Hpp = 0.25$ G. [c] Neither H resolved, $\Delta H_{pp} = 0.5$ G.

in k_1 is actually expected to be considerably smaller than the increase in stabilization since k_1 is not zero when $\theta = 90°$, vide supra. We also discovered[4] that **1c** and **1d** were only 34% and 56%, respectively, as reactive toward ROO· as **1a**. This was also unexpected because **1c** is superior to **1a** in tests simulating food-preserving antioxidant behavior.[7] We now report EPR spectral data for some phenoxyl radicals which throw considerable light on these two unexpected results.

Phenoxyl radicals were generated by UV photolysis of degassed solutions of the phenols in benzene/di-*tert*-butyl peroxide (1:0.2, v/v) at room temperature. Excellent spectra were obtained, and hyperfine splittings (hfs) were derived by comparison with computer-simulated spectra. The data are summarized in Table I. The hfs assignments are based on those of Mukai et al.,[8] which are also given in this table. Our results for the **1b**-derived radical are in good agreement with those of other workers.[8,9] In particular, as Mukai et al.[8] have specifically pointed out, the two H atoms on C-4 are magnetically equivalent.[10] On this basis, these workers suggested that the heterocyclic ring was coplanar with the aromatic ring. However, this is inconsistent with the X-ray structure of **1b**, which shows[3] that the dihedral angle, γ, between the C_3–C_4 bond and the aromatic ring (see **2c**) is 11.1° and 11.9°,[5] i.e., γ is similar in magnitude to θ. The EPR and X-ray data would be consistent if the half-chair to half-chair interconversion of the heterocyclic ring was rapid[11] in solution. However, this "explanation" is rendered highly improbable by the observation that the radical from **1e** shows hfs by only *one* of its two H at position 2—all other hfs being similar to those of the **1b** radical. The heterocyclic ring of the **1e** radical must be conformationally locked[11] with a pseudoaxial H-2 (H_a hfs = 3.30 G) and a pseudoequatorial H-2 (H_e hfs < 0.25 G). Since the two hydrogens in position 4 are equivalent we conclude that *in solution* this radical, and by extension those derived from **1a** and **1b**,[12] adopt a conformation somewhere between a normal half-chair and a type of envelope in which γ is close to zero and θ, as a consequence, is appreciably greater than 16.85°. The parent molecules presumably adopt a similar conformation, see **2a**. This, we believe, provides a simple exlanation for our observation that the antioxidant activity of **3a** is larger relative to **1a** than would be expected on the basis of the X-ray value of θ for **1b**. That is, the crystal and solution conformations of compounds of type **1** are distinctly different.

The reduced reactivity of **1c** and **1d** relative to **1a** or **1b** in their reaction with ROO· was tentatively attributed[4] to the electron-withdrawing carboxyl group, which, by its inductive effect, impairs the ability of the p-type lone pair on the ring oxygen to participate in the delocalization of the unpaired electron and hence in stabilization of the phenoxyl radical. The hfs's found for **1d** (**1c** was too insoluble to give a satisfactory spectrum) provide strong support for this explanation. That is, the decreased spin delocalization by the 1-oxygen in the **1d**-derived radical produces an increase in the spin density on the aromatic ring of about 5%, which manifests itself as a ca. 5% increase in the magnitude of all the H hfs's of **1d** relative to those of the comparable H's in the **1b**-derived radical. Such a change in spin delocalization is, we believe, quite adequate to account for the reduced reactivity of **1d** (and **1c**) toward ROO·. Similarly, we have found that **3b** is only 37% as reactive toward ROO· as is **3a** and that the H hfs's due to the aromatic methyl groups in the **3b**-derived radical are ca. 4% larger than those of the corresponding methyls from **3a**.

Additional kinetic and EPR spectroscopic data that support our conclusions that conformational and polar factors can influence the antioxidant activities of tocopherol model compounds in predictable ways will be presented in a full paper.

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(10) As are those on C-3, which, though not resolved by EPR, were found by ENDOR to have equal hfs of ca. 0.10 G.[8]

(11) On the EPR time scale.

(12) For **1b** this assumption might be checked by labeling both CH_3 groups at the 2-position with carbon-13.

A Remarkable Reversal in the Direction of Boron Migration in the Thermal Isomerization of Organoboranes Derived from 2-Methyl-2-butene

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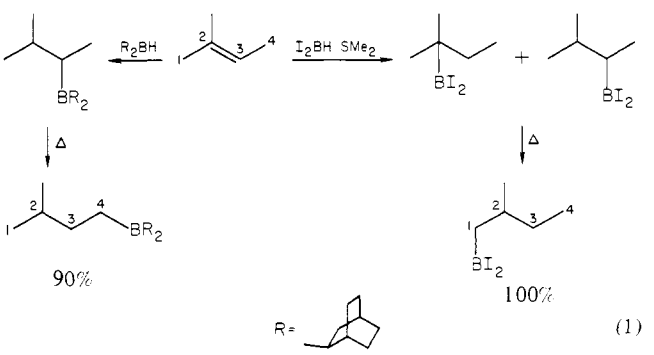
The isomerization of the organoborane derived from 2-methyl-2-butene and bis(bicyclo[2.2.2]octyl)borane proceeds to place 90% of the boron on the carbon C-4, whereas the corresponding derivatives from 2-methyl-2-butene and $I_2BH{\cdot}SMe_2$ undergo isomerization to place 100% boron on the carbon atom C-1 (eq 1). This major reversal in the direction of boron migration



(1)

offers major opportunities for both synthetic application and theoretical interpretation.

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