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

parent phenol	g	a^H, G					ref
		2	4(CH_2)	5(CH_3)	7(CH_3)	8(CH_3)	
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, ΔHpp = 0.25 G. [c] Neither H resolved, ΔH_{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.

Acknowledgment. This work was supported by a grant from the National Foundation for Cancer Research.

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[7] Scott, J. W.; Cort, W. M.; Harley, H.; Parrish, D. R.; Saucy, G. *J. Am. Oil Chem. Soc.* **1974**, *51*, 200–203. Cort, W. M.; Scott, J. W.; Araujo, M.; Mergens, W. J.; Cannalonga, M. A.; Osadca, M.; Harley, H.; Parrish, D. R.; Pool, W. R. *Ibid.* **1975**, *52*, 174–178. Cort, W. M.; Scott, J. W.; Harley, J. H. *Food Technol. (Chicago)* **1975**, *29*, 46–50. Scott, J. W.; Cort, W. M. *Cosmet. Toiletries* **1976**, *91*, 39–44.

[8] Mukai, K.; Tsuzuki, N.; Ishizu, K.; Ouchi, S.; Fukuzawa, K. *Chem. Phys. Lipids* **1981**, *29*, 129–135.

[9] Matsuo, M.; Matsumoto, S. *Lipids* **1983**, *18*, 81–86.

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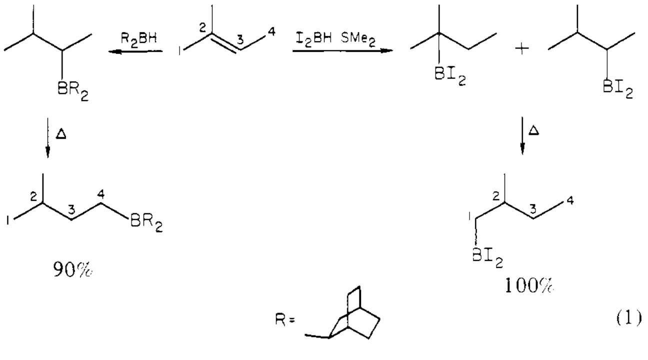
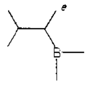
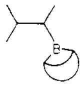
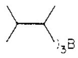
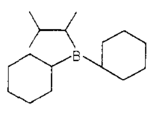
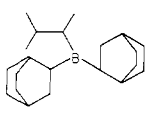
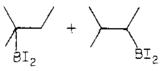
The isomerization of the organoborane derived from 2-methyl-2-butene and bis(bicyclo[2.2.2]octyl)borane proceeds to place 90% of the boron on the carbon C-4, whereas the corresponding derivatives from 2-methyl-2-butene and $I_2BH{\cdot}SMe_2$ undergo isomerization to place 100% boron on the carbon atom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



(1)

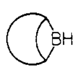
offers major opportunities for both synthetic application and theoretical interpretation.

Table I. Thermal Isomerization of Organoboranes 7–11[a,b] Obtained from 2-Methyl-2-butene at 150 °C[c]

organoborane	time, h	% boron distribution[d] C-1	C-2	C-3	C-4
 [e]	4	40	trace	2	58
 7	264	32	0	0	68
 8	48	17	0	0	83
 9	24	13	0	0	87
 10	4	10	0	0	90
 **11A** (25%) + **11B** (75%)	1	100	0	0	0

[a] No hydride excess was present in any isomerization. [b] The thermal isomerization of trialkylboranes **7–10** was conducted in diglyme but that of **11A** and **11B** was done in *o*-dichlorobenzene. See ref 5. [c] Temperature maintained constantly by a thermowatch. [d] Determined by oxidation and GC analysis. The standard conditions used for the GC separation of alcohols were 10% glycerol on FireBrick (100/120) column (1/8″ × 12′) and isothermal analysis at 60 °C on Varian 1200 FID GC. [e] See ref 6 and 8.

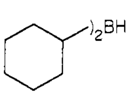
We previously reported the thermal isomerizations of several structurally defined trialkylboranes derived from *cis*-3-hexene at 150 °C and demonstrated that increasing the steric crowding in the initial organoborane remarkably accelerates the rate and significantly improves the equlibrium in favor of 1-alkylboranes.[1-4] More recently, we reported the thermal isomerization of alkyldihaloboranes obtained from *cis*-3-hexene and $HBX_2{\cdot}SMe_2$ (X = Cl, Br, and I) at 150 °C and noted that while the organoboranes derived from $HBCl_2{\cdot}SMe_2$ and $HBBr_2{\cdot}SMe_2$ exhibited a remarkable resistance to isomerization, that obtained from $HBI_2{\cdot}SMe_2$ underwent a facile isomerization.[5] These systematic studies thus afforded a number of monofunctional hydroborating agents **1–5**, which are exceptionally useful from the standpoint



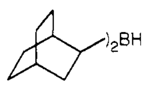
1

$BH_3{\cdot}SMe_2$

2



3



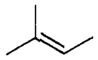
4

$I_2BH{\cdot}SMe_2$

5

of the thermal isomerization reaction. It was therefore of considerable interest to us to expore the full potential of each of the above reagents in the hydroboration–isomerization of structurally representative olefins.

In 1966 it was reported[6] that hydroboration of 2-methyl-2-butene (**6**) with diborane[7] (using 20% hydride excess) followed



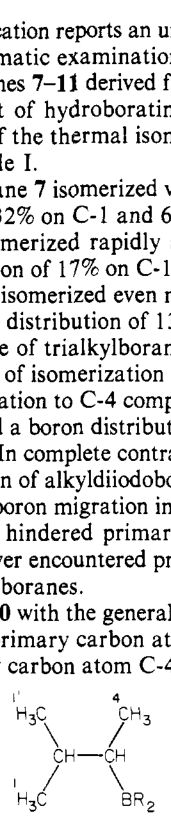
6

by isomerization of the resulting organoborane mixture[8] in refluxing diglyme, resulted in a poorly selective boron migration onto both ends of the alkyl chain (Table I). For the above reasons, 2-methyl-2-butene (**6**) appeared to be an ideal olefinic system to test the potential of the aforementioned monofunctional hydroborating agents.

The present communication reports an unusual boron migration observed during a systematic examination of the thermal isomerizations of organoboranes **7–11** derived from 2-methyl-2-butene (**6**) and the selected set of hydroborating agents **1–5**, respectively.[9,10] The results of the thermal isomerization (at 150 °C) are summarized in Table I.

While the trialkylborane **7** isomerized very slowly and yielded a boron distribution of 32% on C-1 and 68% on C-4 in 11 days, the trialkylborane **8** isomerized rapidly and afforded a highly selective boron distribution of 17% on C-1 and 83% on C-4 in 48 h. The trialkylborane **9** isomerized even more rapidly compared to **8** and yielded a boron distribution of 13% on C-1 and 87% on C-4 in 24 h. In the case of trialkylborane **10**, we observed not only the most rapid rate of isomerization but also the maximum selectivity in boron migration to C-4 compared to C-1. Thus the trialkylborane **10** yielded a boron distribution of 10% on C-1 and 90% on C-4 in just 4 h. In complete contrast to the above results, the thermal isomerization of alkyldiiodoborane mixture **11A** and **11B** resulted in a 100% boron migration in the opposite direction, viz., onto the relatively hindered primary carbon atom C-1, a migratory preference never encountered previously in the thermal isomerization of organoboranes.

In trialkylboranes **7–10** with the general structure **12**, there are two identical terminal primary carbon atoms C-1 and C-1′ and only one unique primary carbon atom C-4 available to boron for



12

migration in the thermal isomerization reaction. If this statistical factor is taken into consideration, then a boron distribution of 10% on C-1 and 90% on C-4 in the thermal isomerization of trialkylborane **10** means that the boron atom prefers C-4 to C-1, nearly 19 times to 1.[11] This is understandable because the terminal primary carbon C-4 is much less hindered than the carbon C-1, and as the size of the substitutent (R) groups on boron increases, the migratory preference by boron for the less-hindered carbon atom C-4 also increases.

On the other hand, the precise reason for the exclusive migratory preference exhibited by the BI_2 moiety for the more hindered carbon atom C-1 in the isomerization of the alkyldiiodoborane mixture **11A** and **11B** is still not clear. However, it is evident that the BI_2 moiety must prefer a relatively crowded hydrocarbon region (see Newman projection formula of the final product below).[12]

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(6) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1966**, *88*, 1433.

(7) Diborane was generated in situ from $NaBH_4$ and $BF_3{\cdot}OEt_2$.

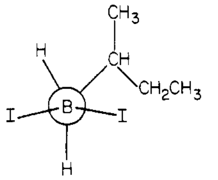
(8) The exact structure of the organoborane was not established. In general, hydroboration of an olefin using diborane (with 20% hydride excess) produces a mixture of di- and trialkylboranes.

(9) The trialkylboranes **7**, **9**, and **10** were prepared by the hydroboration of 2-methyl-2-butene with the dialkylboranes **1**, **3**, and **4**, respectively, at 25 °C in THF. The trialkylborane **8** was prepared by the direct hydroboration of 2-methyl-2-butene with $BH_3{\cdot}SMe_2$ (**2**) taken in a 3:1 molar ratio in THF at 25 °C. The formation of the trialkylborane was checked by ^{11}B NMR in all cases.

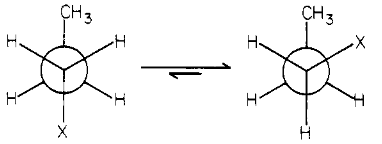
(10) The alkyldiiodoborane mixture **11A** (25%) and **11B** (75%) was obtained by the hydroboration of 2-methyl-2-butene with $HBI_2{\cdot}SMe_2$ (**5**) at 40 °C in CH_2Cl_2 for 1 h.

(11) This is a major improvement over previously reported results (see ref 6 and Table I) wherein the boron atom showed a migrational preference of 3 times to 1 for carbon atom C-4 compared to C-1.

(12) ^{11}B NMR of the final product revealed that the BI_2 moiety was intact.



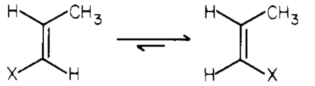
This suggests the operation of stabilizing attractive nonbonded interactions such as those used to account for the greater thermodynamic stability of the "gauche" conformation over the "anti" in 1-halopropanes[13] (eq 2).



(2)

X = F, Cl, Br

A similar interaction has been proposed[14] to account for the greater stability of the "cis" form of the 1-halopropenes[15] over the "trans" (eq 3).



(3)

X = F, Cl, Br

Irrespective of mechanistic considerations, the results of the above study provide, for the first time, a synthetically useful manipulative control on the migrational selectivity of the boron atom. We hope to utilize this for organic synthesis in the future.

Acknowledgment. We are grateful for the financial support of Exxon Research and Engineering Corp. and the National Science Foundation (CHE-8301145).

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(13) (a) Sheppard, N. *Adv. Spectrosc.* **1959**, *1*, 295. (b) Morino, Y.; Kuchitsu, K. *J. Chem. Phys.* **1958**, *28*, 175. (c) Sarachman, T. N. *J. Chem. Phys.* **1963**, *39*, 469. (d) Hirota, E. *J. Chem. Phys.* **1962**, *37*, 283.

(14) (a) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 3087. (b) English, A. D.; Palke, W. E. *Ibid.* **1973**, *95*, 8536. (c) Bingham, R. C. Ibid. **1976**, *98*, 535.

(15) (a) Harwell, K. E.; Hatch, L. F. *J. Am. Chem. Soc.* **1955**, *77*, 1682. (b) Crump, J. W. *J. Org. Chem.* **1963**, *28*, 953.

Stepwise Assembly of Heterometallic M_4S_4 Clusters. The Structure of $(MeCp)_2V_2Fe_2(NO)_2S_4$: A 58e Cubane

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A focus of our research is the development of cluster assembly reactions employing organometallic chalcogenide precursors.[2,3] To a certain extent, this effort parallels related work leading to inorganic sulfide aggregates from MoS_4^{2-}.[4] Recently we reported the preparation of a series of iron carbonyl-containing clusters from $(MeCp)_2V_2S_4$ (**1**, MeCp = η^5-$CH_3C_5H_4$) of core stoichiometries FeV_2S_4, FeV_2S_3, and $PtFeV_2S_4$.[3] Extension of this work to include metal nitrosyls has led to the following achievements: (i) the synthesis of the first electron-deficient organo M_4S_4 clusters, (ii) the characterization of the first closed deltahedral cluster featuring an $M(NO)_2$ vertex, and (iii) the directed synthesis of an $M_2M'M''S_4$ cubane cluster.

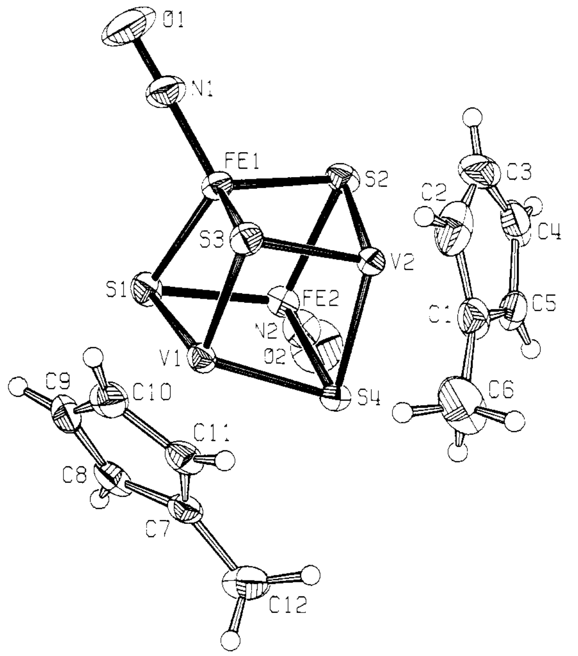

Figure 1. ORTEP plot of the $(MeCp)_2V_2(NO)_2S_4$ molecule with thermal ellipsoids drawn at the 35% level.

Treatment of $(MeCp)_2V_2S_4$[5] with an excess of $Hg[Fe(NO)(CO)_3]_2$ in boiling toluene afforded a 65% yield of $(MeCp)_2V_2Fe_2(NO)_2S_4$ (**2**) as analytically pure black crystals from methanol.[6] Subsequent to chromatography on silica gel, this species was characterized by IR, mass spectrometry, and single-crystal X-ray diffraction.

The results of the X-ray structure analysis[7] established that **2** consists of a distorted $V_2Fe_2S_4$ cubane core (Figure 1). Three types of intermetallic contacts are observed including an Fe–Fe bond of 2.59 Å that is similar to that seen in other S-bridged iron dimers. The four Fe–V bond distances of 2.75 Å are similar if a little shorter than those observed in related compounds.[3] In comparison with the few standards available,[5,8] the V···V distance of 2.95 Å indicates an interaction that is weak but significant; the corresponding distances in the $V_2(\mu$-η^2-$S_2)_2$ subunits of the diamagnetic linear chain compound VS_4 are 2.83 and 3.22 Å.[9] We tentatively conclude that the electron deficiency in **2** is largely associated with the vanadium centers giving rise to longer V–M bonding.

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(5) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.*, in press.

(6) Anal. Calcd for $C_{12}H_{14}N_2O_2S_4V_2Fe_2$: C, 25.72; H, 2.52; N, 5.00; Fe, 19.94; V, 18.19. Found: C, 25.88; H, 2.47; N, 4.91; Fe, 19.79; V, 18.18. IR(CCl_4) 1765 and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) 27.98 (d), 7.75 (s); EI mass spectrum (70 eV), *m/e* (relative intensity) 560 (258 M^+), 530 (20, $M^+ - NO$), 500 (100, $M^+ - 2NO$); field-desorption mass spectrum 560 (M^+).

(7) $(C_5H_4CH_3)_2V_2Fe_2(NO)_2S_4$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.616$ (2) Å, $b = 20.219$ (5) Å, $c = 9.746$ (2) Å, $\beta = 99.16$ (2)° $V = 1870.8$ (7) Å^3, $Z = 4$, $\mu = 28.98$ cm^{-1} (Mo Kα, $\lambda = 0.71069$). A total of 3767 reflections ($3° < 2\theta < 55°$) were collected on a Syntex $P2_1/n$ diffractometer of which 3321 were used. Of these reflections, 2407 with $F_o > 3\sigma(F_o)$ were used in subsequent solution and refinement. $R = 2.3\%$ and $R_w = 2.8\%$.

(8) For a recent partial listing of V–V bond lengths see: Elschenbroich, C.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905.

(9) Allmann, R.; Baumann, I.; Kutoglu, A.; Rösch, H.; Hellner, E. *Naturwissenschaften* **1964**, *51*, 263. Klemm, W.; Schnering, H. G. *Ibid.* **1965**, *52*, 12.

0002-7863/83/1505-6508$01.50/0