stabilized system. Hence, we believe the H_3O bond dissociation energy is probably less than Bernstein's lower limit of 7 kcal/mol.

Our assignment of neutral H_3O rather than $(H_3O)^{2+}$ is based on the following arguments. (1) We would predict $a_H(H_3O)^{2+}$ to be much greater than the 22.84 G observed because, in general, cation radicals display larger splittings than their corresponding anions. For example, $a_H(\text{anthracene})^+ > a_H(\text{anthracene})^-$.[11] This effect is also demonstrated by the isoelectronic series BH_3^-, CH_3, NH_3^+ shown in Table I to which $(H_3O)^{2+}$ would belong. (2) We would expect $(H_3O)^{2+}$ to be a strong oxidizing agent and H_3O a good reducing agent. Hence, the presence of H atoms is more easily correlated with H_3O. (3) We would expect $(H_3O)^{2+}$ to undergo isotopic exchange readily because of its repulsive double charge. However, we observe no enhancement of deuterated species upon continuous irradiation or annealing of the radicals in heavy water. It is remarkable that the esr and exchange properties of H_3O and CH_3 are so similar. If CH_3 is assumed to be planar as claimed,[12] this raises the question of whether H_3O is planar or tetrahedral or partially complexed to another species such as Ce(III).[13] (4) Lastly, we are able to produce H_3O in good yield in basic media, an environment surely more hostile to $(H_3O)^{2+}$ than H_3O.

Table I. Summary of Radicals with Three Equivalent Hydrogens

Radical	a_H or a_D, G	$\bar{g}$	Ref
BH_3^-	16.5	2.0013	*a*
CH_3	23.04	2.00255	*b*
NH_3^+	25.9	2.0035 ± 0.0003	*c*
	25.0	2.0034 ± 0.0001	*d*
H_3O	22.84	2.0035 ± 0.0003	*e*
D_3O	3.65	2.0035 ± 0.0003	*e*

[a] M. C. R. Symons and H. W. Wardale, *Chem. Commun.*, 758 (1967). See also E. D. Sprague and F. Williams, *Mol. Phys.*, **20**, 375 (1971), for interesting temperature effects on $\bar{g}$ and a_H. [b] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). [c] T. Cole, *ibid.*, **35**, 1169 (1961). [d] J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961). [e] This work, with $\bar{g}$ values referenced to diphenylpicrylhydrazyl (DPPH).

In conclusion, we have clearly demonstrated that matrix-stabilized hydronium radicals do exist, and we believe they may become as useful as H atoms and hydrated electrons in understanding water chemistry.

(11) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(12) T. Cole, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *ibid.*, **1**, 406 (1958).

(13) Experiments with ^{17}O water may help resolve these structural questions.

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Hyperfine Interaction of Halide Ions with Metalloporphyrin Cation Radicals

Sir:

Numerous electron spin resonance studies have revealed interactions of diamagnetic cations with aromatic anion radicals.[1] We present here evidence of hyperfine interaction between halogen anions and the cation radical of a metalloporphyrin.

Oxidation of zinc tetraphenylporphyrin (ZnTPP) by controlled-potential electrolysis in CH_2Cl_2, with $(C_3H_7)_4NClO_4$ as carrier electrolyte, results in a stable π-cation radical, $ZnTPP\cdot{}^+ClO_4^-$. This radical is characterized[2-4] by its absorption spectrum and an esr spectrum of nine lines assigned to the four equivalent nitrogens.

Chemical oxidation of ZnTPP in CH_2Cl_2 or $CHCl_3$ with 0.5 mol of Br_2 is reversible[2] and produces a radical with the same absorption spectrum as $ZnTPP\cdot{}^+ClO_4^-$. The esr signal associated with the radical is not, however, the characteristic nine-line spectrum, but consists, instead, of the four lines shown in Figure 1. Similar spectra are obtained if $Co^{III}OEP\cdot{}^{2+}2Br^-$, the cation radical of cobaltic octaethylporphyrin,[3] is used as the oxidizing agent. Treatment of the bromine oxidation product with $AgClO_4$ causes AgBr to precipitate and regenerates the $ZnTPP\cdot{}^+ClO_4^-$ esr spectrum with no change in the absorption spectrum. The number of spins, determined by integration of the esr signals, is conserved within 10%. These facts are consistent with the following equation.

$$\mathrm{ZnTPP} \xrightarrow{0.5\mathrm{Br_2}} \mathrm{ZnTPP}\cdot{}^{+}\mathrm{Br}^- \xrightarrow{\mathrm{AgClO_4}} \mathrm{ZnTPP}\ {}^{+}\mathrm{ClO_4}^- + \mathrm{AgBr}\downarrow$$

The four-line spectrum is thus assigned to hyperfine interaction of the $ZnTPP\cdot{}^+$ radical with one bromide ion (nuclear spin, $I = {}^3/_2$). The experimental spectrum can be simulated assuming the splitting constants of Table I.

Table I. $ZnTPP\cdot{}^+X^-$ in $CHCl_3$

X^-	a_X, G[a]	a_N, G[a]	*g* value
^{79}Br	8.18[b]		
^{81}Br	8.82	1.60[c]	2.0059 (±0.0003)
^{35}Cl	1.66[b]		
^{37}Cl	1.38	1.62	2.0032 (±0.0001)
F	8.78	1.61	2.0027 (±0.0001)
ClO_4		1.46	2.0025 (±0.0001)

[a] Obtained from the computer simulations. [b] Determined by the magnetic properties of the isotopes. [c] From d_{20}-$ZnTPP\cdot{}^+Br^-$ (deuterated phenyl groups), where the nitrogens are partially resolved.

Oxidation of ZnTPP in CH_2Cl_2 or $CHCl_3$ by 0.5 mol of Cl_2, controlled-potential electrolysis with $(C_2H_5)_4NCl$ as supporting electrolyte, or treatment of $ZnTPP\cdot{}^+ClO_4^-$ with excess $(C_2H_5)_4NCl$ all yield a radical with the 12-line esr spectrum shown in Figure 2, but the absorption spectrum remains that of $ZnTPP\cdot{}^+ClO_4^-$. If the solvent, CH_2Cl_2 or $CHCl_3$, is pumped off and replaced by the more polar methanol, the optical spectrum does not change, while the esr spectrum shows the same nine lines as does that of $ZnTPP\ {}^+ClO_4^-$ The 12-line spectrum is satisfactorily simulated assuming hyperfine interaction of $ZnTPP\ {}^+$ with one chloride ion ($I = {}^3/_2$). As previously reported[2] for

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(1) M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967), and references therein.

(2) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).

(3) R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *ibid.*, **91**, 196 (1969).

(4) A. Wolberg and J. Manassen, *ibid.*, **92**, 2982 (1970).

$ZnTPP\cdot^+ClO_4^-$, no hyperfine structure is observed in the presence of oxygen with either ZnTPP + Br^- or $ZnTPP\cdot^+Cl^-$.

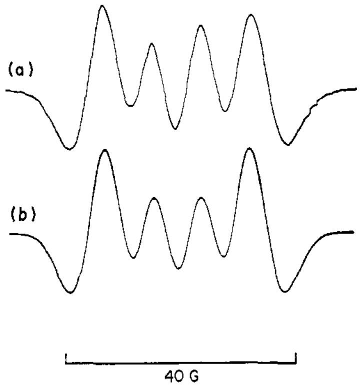

Figure 1. (a) Second-derivative esr spectrum of $ZnTPP\cdot^+Br^-$ in chloroform. (b) Computer simulation: four nitrogens, a_N = 1.60 G; one bromine, $a_{^{79}Br}$ = 8.18 G (50.5%) and $a_{^{81}Br}$ = 8.82 G (49.5%).

Oxidation of ZnTPP with XeF_2 in C_3H_7CN yields a $ZnTPP\cdot^+$ radical, as evidenced by its absorption spectrum.[2] Oxidation with ≈0.5 mol of XeF_2 in CH_2Cl_2 or $CHCl_3$ also results in the same absorption spectrum[5] as before and the esr spectrum shown in Figure 3. The simulation assumes that the nine-line spectrum of $ZnTPP\cdot^+$ is split by one fluoride ion ($I = {}^1/_2$).

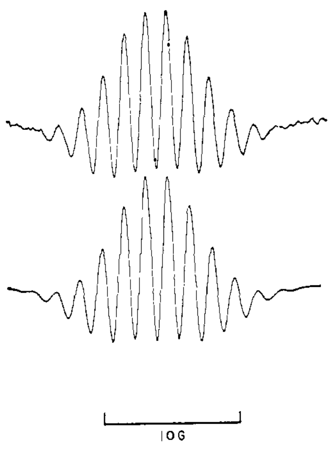

Figure 2. (a) Second-derivative esr spectrum of $ZnTPP\cdot^+Cl^-$ in chloroform. (b) Computer simulation: four nitrogens, a_N = 1.62 G; one chlorine, $a_{^{35}Cl}$ = 1.66 G (75.5%) and $a_{^{37}Cl}$ = 1.38 (24.5%).

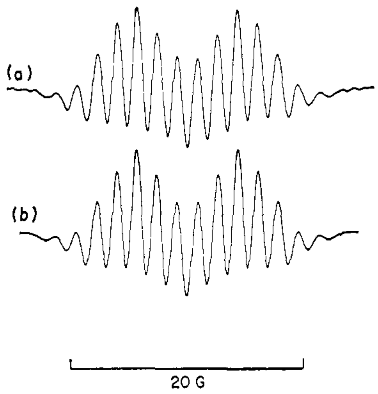

Figure 3. (a) Second-derivative esr spectrum of $ZnTPP\cdot^+F^-$ in chloroform. (b) Computer simulation: four nitrogens, a_N = 1.61 G; one fluorine, a_F = 8.78 G.

Note that a_N is somewhat larger for the halides than for the perchlorate counterion but that the nitrogens remain magnetically equivalent and that the fourfold axis of symmetry of $ZnTPP\cdot^+$ is thus retained. The splitting constants of the halide ions, a_X, are comparable to those reported for halogen-containing radicals.[7–9] The shift in the g values of $ZnTPP\cdot^+X^-$ is consistent with increasing spin–orbit coupling with the heavier halide ion.

Our data suggest that the $ZnTPP\cdot^+X^-$ species should be considered as complexes rather than weak ion pairs. In contrast to ion pairs of anion radicals,[1] no changes in a_X were detected over the concentration and temperature ranges we investigated: ~10^{-3}–10^{-4} *M* $ZnTPP\cdot^+X^-$, 35 to −10° for $ZnTPP\cdot^+Br^-$, and 25 to −40° for $ZnTPP\cdot^+Cl^-$. Neutral ZnTPP itself is complexed[10] by anions (F^-, Cl^-, Br^-, I^-, OH^-) in CH_2Cl_2 and $CHCl_3$. Specific interactions between the charged $ZnTPP\cdot^+$ radical and a halide ion are therefore not surprising in the solvents of low dielectric constants considered here.

We have observed similar halide ion interactions with radicals of MgTPP, CdTPP, and CoTPP. Other effects of gegenions on cation radicals are known. For example, replacement of ClO_4^- by Br^- appreciably shifts the equilibrium between $MgOEP\cdot^+$ or $ZnOEP\cdot^+$ and their dimers.[2,11] Change of Br^- to ClO_4^- (or to BF_4^-) in $Co^{III}OEP\cdot^{2+}$ not only affects the magnetic and optical spectra of the radicals, but, in fact, mirrors the behavior of the porphyrin prosthetic groups in compounds I of catalase and horseradish peroxidase.[12] Thus, besides the intrinsic interest in the mechanism which allows delocalization of spin onto the halide ions, significant effects of gegenions on the chemistry of metalloporphyrin cation radicals can be demonstrated.

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(5) Excess XeF_2 results in an isoporphyrin[2,6] which is diamagnetic and does not interfere with the esr measurements.

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(7) J. Fajer, B. H. J. Bielski, and R. H. Felton, *J. Phys. Chem.*, **72**, 1281 (1968).

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(9) E. F. Ullman and L. Call, *ibid.*, **92**, 7210 (1970).

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(11) J. -H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, **91**, 4174 (1969).

(12) D. Dolphin, A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, *Proc. Nat. Acad. Sci. U. S.*, **68**, 614 (1971).

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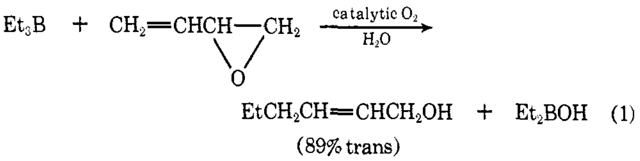
A New Four-Carbon-Atom Homologation Involving the Free-Radical Chain Reaction of 1,3-Butadiene Monoxide with Organoboranes. Synthesis of 4-Alkyl-2-buten-1-ols from Olefins *via* Hydroboration

Sir:

1,3-Butadiene monoxide, which fails to react spontaneously with trialkylboranes, readily reacts in the presence of catalytic amounts of oxygen or other free-radical initiators. This provides a new four-carbon-atom homologation leading to the corresponding 4-alkyl-2-buten-1-ols in relatively high stereochemical purity (eq 1).



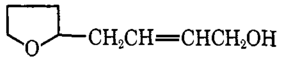
$$\mathrm{Et_3B} + \underset{\mathrm{O}}{\mathrm{CH_2{=}CHCH{-}CH_2}} \xrightarrow[\mathrm{H_2O}]{\text{catalytic } \mathrm{O_2}} \mathrm{EtCH_2CH{=}CHCH_2OH} + \mathrm{Et_2BOH} \quad (1)$$

(89% trans)

We have previously reported that trialkylboranes, readily available *via* hydroboration, undergo a "spontaneous" 1,4 addition to numerous α,β-unsaturated carbonyl compounds including methyl vinyl ketone,[1a] isopropenyl methyl ketone,[1b] acrolein,[1c] α-methylenecyclanones,[1d] and 2-methyl- and 2-bromoacrolein.[1e] Other derivatives, such as *trans*-crotonaldehyde, *trans*-3-penten-2-one, 2-cyclohexen-1-one, and acetylacetylene, failed to react spontaneously, but reacted quite readily through photochemical sensitization[2a] or by catalysis with typical free-radical initiators, such as acyl peroxides,[2a] azobisisobutyronitrile,[2b] and oxygen.[2b,c] Thus, these 1,4 addition reactions apparently proceed by a free-radical chain mechanism since they are promoted by typical free-radical initiators and are inhibited by free-radical scavengers, such as galvinoxyl.[1b]

No reaction occurs between 1,3-butadiene monoxide and triethylborane in the absence of oxygen. However, the reaction proceeds nicely with the introduction of small quantities of air.

Since trialkylboranes are generally prepared as tetrahydrofuran (THF) solutions, THF has normally been the solvent of choice for such 1,4 addition reactions. Unfortunately, in the present case we observed in this solvent the formation of considerable quantities of 4-(2′-tetrahydrofuryl)-2-buten-1-ol[3] (**1**) accompanying the formation of the desired product. The reaction evidently involves free-radical intermediates and the free-radical addition of THF to the epoxide takes place competitively. This side reaction could be avoided with benzene as the solvent.



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Under these conditions, the yield of 2-hexen-1-ol was 44% with equal molar amounts of monoxide and triethylborane, but improved significantly with increasing molar ratios of monoxide to borane (see Table I). Indeed, quite satisfactory yields could be realized with excess monoxide (Table I). The 2-hexen-1-ol[4] was predominantly the trans isomer, 89% trans, 11% cis. This ratio was insensitive to both the temperature and the monoxide concentration.

Table I. Oxygen-Induced Addition of Organoboranes to 1,3-Butadiene Monoxide[a]

Borane	Molar ratio (epoxide/borane)	4-Alkyl-2-buten-1-ol[b] yield,[c] %		$n^{20}\mathrm{D}$, deg
		Benzene (trans/cis)	Diethyl ether	
Triethyl	1	44 (89/11)		1.4363
Triethyl	1.5	58 (89/11)		
Triethyl	2	68 (88/12)		
Triethyl	3	75 (89/11)	65	
Tri-*n*-butyl	3	73[d]	66[d]	1.4465
Triisobutyl	3	44	53	1.4433
Tricyclopentyl	3	46	56	1.4777
Tricyclohexyl	3	45	61	1.4811

[a] The reactions were conducted at 25° using 5 mmol of organoborane in 5 ml of solvent and adding air at the rate of 1 ml/min. [b] All alcohols were characterized by nmr and ir spectra, refractive index, and elemental analysis. [c] Based on 5 mmol of organoborane. [d] The product was composed of a 93:7 mixture of straight and branched chain isomers, respectively. [e] These values are in good agreement with those reported by E. S. Huyser and L. R. Munson, *J. Org. Chem.*, **30**, 1436 (1965).

Typical free-radical initiators, such as di-*tert*-butyl peroxide and azobisisobutyronitrile, as well as oxygen, are also effective in promoting the reaction. Moreover, a typical free-radical scavenger, galvinoxyl, inhibits the reaction. Thus, this reaction must involve a free-radical chain mechanism.

Trialkylboranes react with oxygen[5] and *tert*-butoxy radicals[6] to generate alkyl radicals (eq 2). In the presence of 1,3-butadiene monoxide, these alkyl radicals must add to the double bond of the epoxide to yield an

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(1) (a) A. Suzuki, A. Arase, H. Matsumoto, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967); (b) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *ibid.*, **92**, 710 (1970); (c) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (d) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968); (e) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).

(2) (a) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712 (1970); (b) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92** 3503 (1970); (c) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970).

(3) All products were isolated and characterized by nmr, ir, and elemental analysis.

(4) The infrared spectrum of each 4-alkyl-2-buten-1-ol prepared in the present study exhibits a strong band at ~980 cm^{-1} indicating that the trans isomer is the predominant component. The cis/trans ratio of 2-hexen-1-ol was determined by comparison of the glpc trace obtained on a 12-ft 5% Quadrol column with those of authentic mixtures of the cis and trans alcohols.

(5) (a) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969); (b) P. G. Allies and P. B. Brindley, *ibid.*, 1126 (1969); (c) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971).

(6) A. G. Davies and P. B. Roberts, *Chem. Commun.*, 699 (1969).