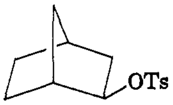
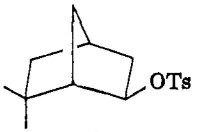
Analysis of the Rate Retardation by 6 Substituents in *exo*-Norbornyl Solvolyses[1]

Sir:

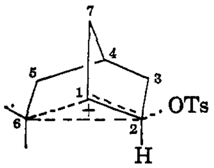
The 25-fold diminution in *exo-p*-toluenesulfonate acetolysis rate that results from changing the norbornyl (**1**) structure to 6,6-dimethylnorbornyl (**2**) has been ascribed[2] to "unfavorable methyl group steric interactions, with both C-1 and C-2 in a nonclassical transition state (**3**)." It is estimated[2,3a] that acetolysis of **2** is anchimerically assisted by at most a power of ten, whereas the acceleration factor in **1** is 3.3 powers of ten. This method of estimating the effect, like any rate comparison using different substrates, requires analysis of influences in both ground states and both transition states. It would be desirable to know the extent to which the steric effect interferes with the normal stabilization *in the transition state alone.* To this end, we have investigated the capture by solvent of the methylnorbornyl cations, reactions that are (to a good approximation) the microscopic reverse of the solvolyses. Table I gives the results.



1

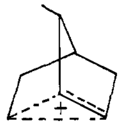


2

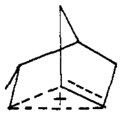


3

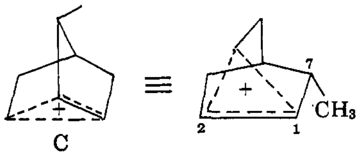
The product ratios from cations A and B,[4] where the lone methyl group is remote from the reaction site, serve as calibration points. In each case the two Wagner–Meerwein-related products are formed in virtually equal amounts under all conditions and from three different starting materials. As expected, the steric effect of the remote methyl group is negligibly small. Cation C, however, shows a pronounced preference for forming the *syn*-7-methyl-2-*exo* rather than the 3-*exo*-methyl-2-*exo* product, in accord with the expected less severe shielding of C-2 than of C-1 by the 7-methyl.



A

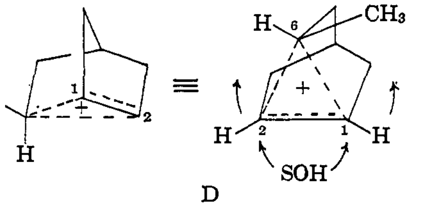


B



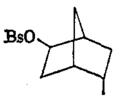
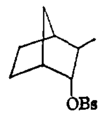
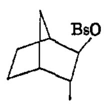
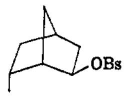
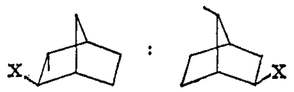
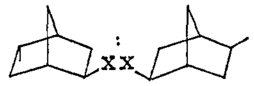
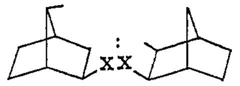
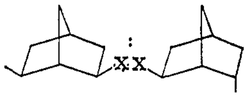
C

In cation D, even though the methyl group now does not interfere directly with the line of approach of solvent (SOH) to the *exo* side of either C-1 or C-2, there is an 8- to 10-fold preference for attack at C-2, leading to the 6-*exo*-methyl-2-*exo* rather than the 6-*endo*-methyl-2-*exo* product. One interpretation of the



D

Table I. Products Derived from Capture of Methylnorbornyl Cations

Wagner-Meerwein pair[a]	Cation	Starting material and conditions[b]  HOAc	 HOAc	aq EtOH	 HOAc	aq dioxane	 HOAc	aq EtOH
		Product ratio[c]						
	A	1.15	1.05	1.13	1.03	0.98		
	B	1.33	1.13	1.30	1.1	1.4		
	C		5 ± 0.5	4 ± 0.5				
	D						9.9	8.1

[a] In acetolyses, X = OAc; in aqueous ethanol or aqueous dioxane, X = OH. [b] Acetolyses at 95–100°, NaOAc buffered; hydrolyses at 95°, pyridine buffered. [c] Product ratios do not change under reaction conditions. All new compounds reported give satisfactory microanalyses. In each case, other products are formed and will be described elsewhere.

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(1) Support of part of this work by the National Institute of Arthritis and Metabolic Diseases, through Grant No. AM-07505, and by the National Science Foundation is gratefully acknowledged.

(2) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem Soc.*, **87**, 375 (1965).

(3) (a) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964); (b) *cf.* C. S. Foote, *ibid.*, **86**, 1853 (1964).

(4) For other aspects of the chemistry of cations A and B, see (a) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **87**, 3246 (1965); (b) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, **87**, 3248 (1965).

preference is based on the repulsive interactions which develop in the transition states. An important one of these involves the site of attack, where a hydrogen is driven upwards toward either another hydrogen or a methyl group at C-6. It seems reasonable to assume that the H-CH_3 repulsion generated during attack at C-1 would be the more serious one, and that consequently attack at C-2 would predominate.

The steric effect in the product-forming step is ascribed to a transition-state free-energy difference alone, since the ground states are either the same or effectively the same (a common nonclassical ion D, or if the opponents of such species insist, a pair of rapidly equilibrating classical ions). Whatever its detailed nature, a kind of specific destabilization similar to that in the transition state leading to the 6-*endo*-methyl-2-*exo product* must also be present in the solvolysis of a corresponding 6-*endo*-methyl-2-*exo substrate.* The present results provide experimental evidence that transition-state steric effects account for part of the observed[2] retardation in the 6,6-dimethyl case.

(5) National Institutes of Health Predoctoral Fellow, 1964-1965.

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Polyhedral Borane Free Radicals[1]

Sir:

When the reaction of $CuCl_2$ with $K_2B_{10}H_{10}$ in organic solvents was first reported,[2] the paramagnetic species was presumed to be a copper(II)-cage complex. We wish to present evidence that in this and other hitherto unreported reactions, oxidation of polyhedral boranes produces true free radicals.

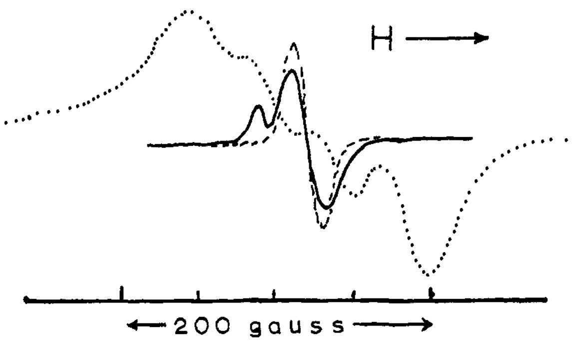

Figure 1. The esr spectra of radicals derived from $B_{10}H_{10}^{-2}$ (solid line) and $B_{20}H_{17}OH^{-4}$ (dashed line), both in isopropyl ether, compared with that of anhydrous $CuCl_2$ in tetrahydrofuran (dotted line); all concentrations *ca.* 10^{-3} *M.*

Anhydrous $CuCl_2$ oxidizes $B_{10}H_{10}^{-2}$, $B_{20}H_{17}OH^{-4}$,[3] partially halogenated, and other cage-substituted systems to free radicals in over 30 organic solvents containing oxygen or nitrogen. Of these, alkyl ethers give the most stable and purest (free of starting materials) solutions of the radical. Solutions in ethyl acetate or tetrahydrofuran, for example, are invariably contaminated with $CuCl_2$. In a typical preparation anhydrous ether is added to a finely ground mixture of $K_2B_{10}H_{10}$ and anhydrous $CuCl_2$; the mixture is stirred until it is dark violet-blue and filtered. In addition to the radical, such solutions contain traces of CuCl and varying amounts of HCl and radical decomposition products. A purple to wine-red color is a sign of extensive decomposition. Alkali, amines, and reducing agents such as I^- and BH_4^- rapidly destroy the radical. When $FeCl_3$ is used, ketones, alcohols, esters, and nitriles have been found to work best, even though in such solvents the radical seldom lasts more than a few minutes at room temperature.

That $B_{10}H_{10}^{-2}$ and $B_{20}H_{17}OH^{-4}$ yield such similar radicals is significant and suggests that in contrast with $B_{20}H_{18}^{-2}$, where electrons appear free to move between cages,[4] systems joined through a B-B bond remain electronically isolated, which confines the spin to one cage. The visible spectrum of every radical so far investigated consists of a single band between 17,000 and 19,000 cm^{-1} with a half-width of 3000 cm^{-1}. Since its molar extinction coefficient is about 3000 and the frequency depends on concentration and solvent polarity, it is undoubtedly a charge-transfer band. In ethereal solutions, which obey Beer's law, good correlation exists between boron content and absorbance at 18,000 cm^{-1}. No such correlation could be established for copper whose concentration, as determined by flame photometry, in isopropyl ether solutions of unit absorbance (1-cm path length) varied from 2×10^{-5} to 2×10^{-4} *M.* In general, solutions of radical derived from $B_{10}H_{10}^{-2}$ contained more copper than did those of radical produced from $B_{20}H_{17}OH^{-4}$, which might account for the presence of the secondary low-field peak in the esr spectra of the former (Figure 1); though the nature of this peak is still under investigation, variations in its relative intensity and the larger *g* value favor the assignment of the peak to a soluble copper(II)-cage complex.

Table I. Physical Properties of Borane Radicals

Source	Medium	*g* value	$\Delta H/2$, gauss[a]	$\nu \times 10^3$, cm^{-1} [b]
$K_2B_{10}H_{10}$ and $CuCl_2$	Acetic acid	2.020	21.4	18.5
	Isopropyl ether	2.0202	22.0	18.0
	Tetrahydrofuran	2.0183[c]	36.0[c]	17.8
$K_2B_{10}H_{10}$ and $FeCl_3$	Methanol	...	...	17.5
	Acetonitrile	2.021	...	17.8
	Ethyl acetate			18.2
$K_4B_{20}H_{17}OH$ and $CuCl_2$	Isopropyl ether	2.0166	23.7	18.4

[a] These are dimensions at room temperature. At 77.4°K the bands are twice as wide. [b] For absorbance <1 and 1-cm path length. [c] In this solvent the principal peak and the shoulder 25 gauss downfield (Figure 1) were not resolved.

Shaking ethereal solutions with hydrochloric acid solutions of $(CH_3)_4NCl$ precipitates salts of hydroxy-

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(1) Research sponsored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

(3) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

(4) A. Kaczmarczyk and G. B. Kolski, *ibid.*, **4**, 665 (1965).