vated aminoborane. Boron–alkyl photocleavage has no parallel in the solution-phase photochemistry of stilbenes[9] and olefins. Superficially, the boron–alkyl scission resembles the α-cleavage reaction of ketone photochemistry and fragmentation β to an amino function observed in the mass spectrometer. Both the quantum efficiency for boron–alkyl cleavage and the chemical yield of alkyl–trichloromethyl radical coupling products decrease in the order benzyl, isopropyl, and ethyl, roughly reflecting the stability of the alkyl radical being generated. The generally low quantum yields of boron–alkyl cleavage were to be expected in light of our recent demonstration that photochemical cis–trans isomerization of aminoboranes is an efficient ($\Phi \sim 0.4$) deactivation mechanism.[10]

One further conclusion can be drawn from our work. Similar bicoordinate aminoboryl radicals have been previously implicated[5,11] as reaction intermediates in the photochemistry of bis(amino)diborane(4) diene analogs. Recombination of such radicals was proposed as one possible, but undemonstrated, decay mechanism. The absence of bis(methylphenylamino)-diphenyldiborane(4) in detectable amounts as a photoproduct of (*N*-methylanilino)alkylphenylboranes suggests that coupling of boryl radicals is not an efficient process.

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Bond Energy Ordering by Isotope Effects and the Structure of Substituted 2-Bromoethyl Radicals[1]

Sir:

The relationship between bond strengths and isotope effects in hydrogen atom transfer, long understood qualitatively,[2] has been recently put on a more quantitative basis.[3,4] The earlier work on addition of mercaptans to olefins[4] is here extended to the free radical chain addition of hydrogen bromide.

The isotope effect is determined in the hydrogen transfer step

$$\mathrm{R\dot{C}HCH_2Br + \overset{*}{H}Br \longrightarrow RCH\overset{*}{H}CH_2Br + Br\cdot} \qquad (1)$$

The tritium isotope effects, measured as the ratio of specific molar activity of hydrogen bromide divided by that of the addition product, $\mathrm{RCH_2CH_2Br}$, when the addition is done in the presence of a large excess of trace tritium labeled HBr,[5] are presented in Table I for various substituents R.

Table I. Isotope Effects in the Radical Addition of HBr to $\mathrm{RCH{=}CH_2}$

R	$k_{\mathrm{H}}/k_{\mathrm{T}}$[a]
p-Tolyl	1.04, 1.03[b]
Phenyl	1.46, 1.47[c]
p-Chlorophenyl	1.55, 1.62[d]
tert-Butyl	1.99, 1.99[e]
n-Hexyl	2.07, 2.07[e]
Br	2.83[e]
H	4.14, 4.25[f]

[a] Duplicate results shown when done. All experiments in diethyl ether solution at 0°, initiated by photolysis of azobisisobutyronitrile. [b] Product counted as crystalline pyridine derivative, *N*-2-*p*-tolylethylpyridinium bromide, mp 179–181°. [c] Counted as pyridinium salt, mp 178°. [d] Counted as pyridinium salt, mp 151–153°. [e] Counted as such after gc purification. [f] Converted *via* the Grignard reagent and phenyl isocyanate to propionanilide, mp 103–104°, for counting.

In one respect the results confirm the results with the mercaptan addition, for the order of increasing isotope effects in the table is also the expected order for increasing strength of the forming CH bond, or decreasing stability of the analogous radical $\mathrm{R\dot{C}HCH_3}$. However, the quantitative interpretation of the isotope effects, both with respect to the lack of a maximum and the very small magnitude,[6] requires special consideration, which we attribute to two factors: (1) the fact that HBr is diatomic, and (2) the special influence of the β-bromine. We have experimentally shown that the small isotope effects are not a consequence of isotopic equilibration of the product and the labeled hydrogen bromide.

The special effect of a diatomic reagent appears in any complete treatment of isotope effects[7–9] but is not a feature of simplified treatments which are successful with most molecules. Two factors left out of the simplified treatments are, first, HBr and TBr differ in moments of inertia by a factor of 3, and, second, there are two perpendicular bending modes in any transition state for attack on HBr uncompensated by any bending vibration in the reagent. The latter factor is in the opposite direction from normal isotope effects and is responsible for the low values of the isotope effect. The isotope effects arising from these two special sources are conveniently illustrated for the reaction $\mathrm{BrH + \cdot Br \rightarrow Br\cdot + HBr}$ for which the isotope effects neglecting tunneling can be exactly calculated by Melander's equations 2–5[8] for various values of the frequency of the doubly degenerate transition state bending vibration, $\nu_{\mathrm{H}}{}^{\ddagger}$, the only unknown for this symmetric system. Thus at 0°, $k_{\mathrm{H}}/k_{\mathrm{T}} = 49.5$, 11.5, 7.1, 3.2, and 1.7 for $\nu_{\mathrm{H}}{}^{\ddagger} = 0$, 500, 800, 1200, and 1500 cm^{-1}, respectively. The last value of $\nu_{\mathrm{H}}{}^{\ddagger}$ is unreasonably high, being even greater than the corresponding frequency of the bihalide ions, which have an electro-

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static restoring force. If we then believe that $k_H/k_T = 1.7$ is an extreme lower limit for the isotope effect in a symmetrical hydrogen transfer, we must conclude that the transition states for the first three entries in Table I are unsymmetrical and contain a substantial amount of isotope dependent symmetric stretch zero-point energy. The inclusion of a tunnel correction merely strengthens the argument. In contrast to this conclusion, the benzylic carbon–hydrogen bond and the HBr bond have about the same energies (*ca.* 87 kcal/mol),[10] so that the cases of R = aryl would appear to be those with the least zero-point stretching vibration. These two contrary conclusions can be reconciled if the β-bromine (by virtue of a neighboring group participation) stabilizes the radicals and weakens the CH bond. Thus the maximum in the isotope effect from the stretching vibrations alone will not come at R = aryl but should come farther down the table. We cannot conclude that the maximum in fact occurs at R = H, nor can we guess which side of the maximum this point lies. It is only certain that the CH bond in ethyl bromide is the strongest one of the group.

The isotope effects thus show that the neighboring bromine lowers the energy of substituted β-bromoethyl radicals, possibly by formation of a cyclic species analogous to the bromonium ion in carbonium ion chemistry. This result is in complete agreement with those based on stereochemical arguments[6,11] and also those based on rates of bromine atom attack on alkyl bromides,[12-14] despite questions about some of the early results.[15]

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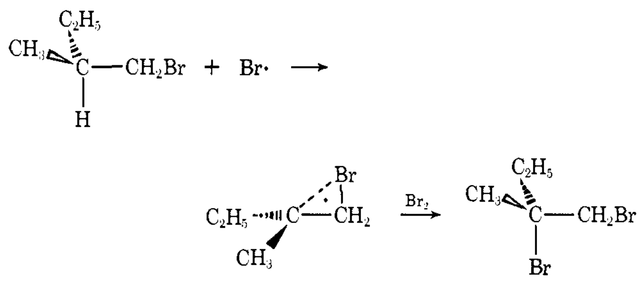
Stereospecific Radical-Chain Exchange of Hydrogens

Sir:

Among the infrequent instances in radical chemistry of retention of antipodal purity at the radical site are those in which a bromine or chlorine atom is located β to the radical site.[1] These observations have been explained with the postulate of an intermediate in which the halogen atom serves as a bridge. The postulate is illustrated for the photobromination of (+)-1-bromo-2-methylbutane.

Earlier, trapping of optically active bridged intermediates has been accomplished with bromine,[1a] *t*-BuOBr,[1b] and *t*-BuOCl.[2] We report here the successful trapping of a dissymmetric intermediate with DBr, resulting in addition of a deuterium to the radical center with >96% retention of the original skeletal configuration.



A solution of (+)-1-bromo-2-methylbutane (13.2 mmol, $[\alpha]^{27}\mathrm{D}$ $+3.99^\circ$ neat), bromine (4.0 mmol), and deuterium bromide (57 mmol) in trichlorofluoromethane (5 ml) was irradiated (GE A-H6 lamp, soft glass filter) at 0° in a sealed tube (dead space *ca.* 15 ml). Irradiation was discontinued when the bromine color was discharged, after 20 min. Analysis by glc showed a single product, 1,2-dibromo-2-methylbutane, as had been reported previously.[1a] Preparative glc separated "unreacted" 1-bromo-2-methylbutane, $[\alpha]^{21}\mathrm{D}$ $+3.95^\circ$ (neat). Mass spectrometric analysis (P and P − Br) showed the recovered monobromide to contain 51.8% d_1. The site of deuterium incorporation was established by dehydrohalogenation (DMSO-$(CH_3)_3COK$) which yielded 2-methyl-1-butene-d_0.[3,4]

Further dilution of reactants with trichlorofluoromethane does not significantly affect the results. Thus, photobromination of active amyl bromide, $[\alpha]^{21}\mathrm{D}$ $+3.95^\circ$, with bromine (4 mmol), in the presence of DBr (36 mmol) in trichlorofluoromethane (30 ml), yields "unreacted" 1-bromo-2-methylbutane, $[\alpha]^{23}\mathrm{D}$ $+3.83^\circ$, 54.2% d_1.

This experiment shows that in radical substitutions of deuterium for hydrogen in (+)-1-bromo-2-methylbutane (1) substitution occurs exclusively at C-2, (2) the sign of rotation is unchanged, and (3) the magnitude of the rotation is very little affected despite the high degree of conversion in a reversible reaction.

Whereas in the case of bromine substitution relating configuration and optical purity for starting material and product was difficult to accomplish, in this instance the correlation is almost trivial, since the substitution of H for D can have only a minor effect on the magnitude of rotation.[5]

Consequently, this experiment demonstrates the high degree of retention of configuration required by the bridging hypothesis (see Scheme I).[1]

A number of alternative explanations of the formation of optically active products in photohalogenations such as cage effects[6] or asymmetric induction[7] cannot explain the high degree of retention of antipodal purity which is observed for radical trapping by a *noncage reagent*, DBr.

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(2) D. C. Lewis, unpublished results, The Pennsylvania State University. Active 2-bromobutane was converted to active *erythro-* and inactive *threo*-2-bromo-3-chlorobutane.

(3) Exchange did not occur in the dehydrohalogenation system. When 1-bromo-2-methylbutane-d_0 was treated under the same conditions with DMSO-d_6 and $(CH_3)_3COK$, 2-methyl-1-butene-d_0 was obtained.

(4) A limit of <2% was placed on the deuterium analysis.

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