ethylene from attack of Grignard on solvent.[35] The spectra of the other two Grignards showed similar behavior, except that the *m*-trifluoromethyl case had olefinic resonances of Grignard and hydrocarbon at 6.67 and 6.40 ppm, respectively.

Hydrolysis of the Grignard reagent from 4-chloro-1-phenylcyclohexene yielded a single major component on gas chromatography. It was collected preparatively, and the structure was confirmed as 1-phenylcyclohexene by comparison of its ir and nmr spectra with spectra of authentic samples.[36,37] A smaller peak eluted later coincided in retention time with biphenyl. Its importance increased somewhat at long heating times. With heating, a small peak of shorter retention time (originally *ca.* 1%) increased in size. The collected sample had the following nmr spectrum: δ 7.2 (m, 5, aryl), 5.80 (q, 1, $J \sim 1$ Hz, olefinic), 3.2–1.2 (m, 5), and 1.07 ppm (d, 3, $J = 6.5$ Hz, methyl). The spectrum is appropriate for the expected product, 3-methyl-1-phenylcyclopentene. For comparison, a mixture of 3-methyl-1-phenylcyclopentene and 4-methyl-1-phenylcyclopentene was prepared by addition of phenylmagnesium chloride to 3-methylcyclopentanone, followed by dehydration as described above for other syntheses.[38] Gas chromatography failed to give sufficient resolution of the components for a preparative separation, but did indicate very slight separation into components. The retention time coincided with that of the component from the Grignard hydrolysis. The nmr spectrum was also generally similar to that of the Grignard hydrolysis product, but showed differences in intensity in the 3.2–1.2 ppm range. These are consistent with the presence in the mixture of 4-methyl-1-phenylcyclopentene, which should lack nonallylic methylene absorption in the vicinity of δ 1.6 ppm, and which is also an expected dehydration product.

Hydrolysis products from the other two Grignard reagents showed a similar pattern, except that the *m*-trifluoromethyl compound appeared to rearrange somewhat more rapidly, and show a greater maximum degree of rearrangement, while the *p*-methyl compound rearranged less readily. Spectra of products were quite similar to their analogs in the unsubstituted phenylcyclohexenyl system. It was found that in mixed runs involving the *m*-trifluoromethyl compound as one component, the yield of biphenyl from the other component (*p*-methyl or unsubstituted phenyl) was particularly high (15–20% before heating), although *m*-trifluoromethylbiphenyl was never great (2–3%); biphenyl yield in the absence of trifluoromethyl compounds was low (3–4%). An authentic sample of *m*-trifluoromethylbiphenyl[38,39] was prepared for gas chromatographic comparison.

Additional evidence of proton abstraction by Grignard reagent under vigorous and extended heating was provided by hydrolysis of the Grignard reagent with D_2O. 1-(*m*-Trifluoromethylphenyl)cyclohexene, isolated from an unheated sample of Grignard reagent, was found by mass spectrometric analysis to be 82% monodeuterated. However, after 48 hr at 125–130°, only 10% of this component was deuterated, and the hydrolyzed rearrangement product, 3-methyl-1-(*m*-trifluoromethylphenyl)cyclopentene, was 25% monodeuterated.[40]

Kinetics. Grignard solutions were prepared from mixtures of two halides in approximately equal concentration, with total concentration of Grignard about 0.3–0.5 *M*. Grignard solutions were analyzed after hydrolysis by titration for total base and for magnesium. With Grignard reagent mixtures including the m-CF_3 compound, the magnesium titration gave values about 20% higher than the total base, suggesting the likelihood of some disproportionation process occurring during Grignard formation. Samples were heated in sealed tubes for appropriate periods of time in a bath controlled to 122 ± 0.3°. After hydrolysis, samples were analyzed by gas chromatography for the hydrocarbon corresponding to both rearranged and unrearranged Grignard reagents. Equal detector response of isomers was assumed. In the comparison of *p*-methyl with *m*-trifluoromethyl, the gas chromatographic separations were completely clean and led to the most reliable relative reactivities; in the other two comparisons, there were some near coincidences of retention times that required a resolution of partially overlapping peaks. Most gas chromatographic analyses were done in duplicate, with good agreement between duplicate determinations.

First-order plots [log (fraction unrearranged) *vs.* time] were curved. Such behavior is anticipated if destruction of Grignard is competitive with rearrangement. Rough initial rates were determined from these plots. In earlier runs carried further to completion, the fraction of rearranged hydrolysis product reached a maximum, and then decreased with further heating. Relative rates were obtained as the slope of a plot for one compound *vs.* the other in a comparison run of either (fraction rearranged) or log (fraction unrearranged). These plots were linear, within the limits imposed by scatter in the data, and gave substantially identical slopes and statistical parameters. Slopes, standard deviations, and correlation coefficients were evaluated by an unweighted least-squares analysis.

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(37) An nmr spectrum of authentic 1-phenylcyclohexene was kindly supplied by Mrs. A. Napiorkowski of the Aldrich Chemical Co.

(38) We acknowledge the assistance of Mr. M. Schwiesow who carried out this preparation.

(39) C. K. Bradsher and J. B. Bond, *J. Amer. Chem. Soc.*, 71, 2659 (1949).

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Anchimeric Assistance in Photobromination of Alkyl Halides

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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received April 10, 1973*

Abstract: Anchimeric assistance approaching 10^3 in magnitude is observed in photobromination of alkyl bromides. This is attributed to bromine assistance in the transition state with the requirement of an antiperiplanar arrangement of the bridging bromine and the hydrogen being abstracted by a bromine atom. Also, the activation energy is lower and activation entropy more negative than for the photobromination of alkanes as required by the bridging mechanism. Alkyl chlorides and fluorides do not show an anchimeric assistance effect. Conditions are described for photobromination with constant bromine concentration (bromostasis) and complete scavenging of hydrogen bromide.

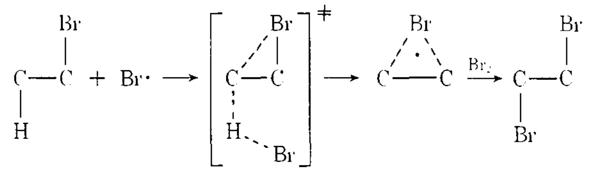
There have been a number of studies on the influence of an electronegative substituent on the rate of hydrogen abstraction by halogen atoms. Generally, electronegative substituents deactivate, the effect attenuating with separation of the reaction site and substituent.

As illustration, liquid-phase chlorination of 1-chloro-[1] and 1-bromobutane[2] showed that the 2 position is *ca.* 0.5 times as reactive as the 3 position.[3,4] The same relative reactivity pattern is found for bromination of alkyl chlorides.[5] The bromination of 1-bromobutane produced a startling result: the 2 position is almost six times as reactive as the 3 position.[2]

Earlier reports[6] of such anomalous activation were shown to be due to ionic reactions.[7] However, the activation for bromine substitution at a position β to a bromine substituent is found in several cases and has been observed in the absence of ionic complications.[2,8,9]

The activation of the β position in brominations of alkyl bromides was interpreted in terms of neighboring group participation (anchimeric assistance). Apparently the larger and more easily polarizable bromine substituent is more effective than chlorine in assisting β-hydrogen abstraction.

The stereochemical consequence of anchimeric assistance by a β-bromine substituent has been indicated to require an antiperiplanar configuration of the H–C–C–Br portion of the molecule. In all cases where anchimeric assistance is observed, control of stereochemistry of the product to give retention of configuration is observed.[10,11] These are rationalized with bromine substituent participation in both the transition state and the intermediate, followed by backside displacement on the intermediate by bromine.



Bromine assistance effects are prominent in photobrominations involving abstractions by Br· but play minor roles in halogenations with Cl· or *t*-BuO·; the larger the activation energy of the abstraction step, the more effective is the assistance by a neighboring bromo substituent.[10,11a]

The present report is concerned with the magnitude of the anchimeric effect, determined by competitive brominations of closely related substrates. However, the interpretation of such experiments is not free from ambiguities. When hydrogen abstractions are endothermic, the reaction is readily reversed. To avoid the complexities of interpretation which can be introduced if the hydrogen abstraction step is reversible,[12] it is necessary to employ efficient scavenging of hydrogen bromide, thus precluding the reversal process. This was

$$\mathrm{RH + Br\cdot \rightleftarrows R\cdot + HBr}$$

best accomplished by including *N*-bromosuccinimide in the system since, as will be shown, the reaction of NBS with HBr to produce Br_2 is rapid and complete.

Bromostasis

Reaction of Hydrogen Bromide with *N*-Bromosuccinimide. There is compelling evidence for a bromine atom chain reaction in *N*-bromosuccinimide brominations of aromatic,[16] allylic,[17] and aliphatic[18] substrates. The bromine atom chain reaction is believed to be initiated by trace amounts of bromine or acidic impurities in the *N*-bromosuccinimide. The

$$\mathrm{Br_2 \xrightarrow{h\nu} 2Br\cdot} \tag{1}$$

$$\mathrm{RH + Br\cdot \longrightarrow R\cdot + HBr} \tag{2}$$

$$\mathrm{R\cdot + Br_2 \longrightarrow RBr + Br\cdot} \tag{3}$$

$$\mathrm{HBr + NBS \longrightarrow Br_2 + succinimide} \tag{4}$$

evidence indicates that a succinimidyl radical does not participate in the reaction sequence, but rather NBS serves as a reservoir for molecular bromine.

This scheme indicates a method for carrying out a bromine substitution reaction at constant bromine concentration, *bromostasis.* For useful bromostasis the reaction of HBr with NBS must be fast and complete.

Pearson and Martin[16d] reported the reaction of hydrogen bromide with NBS is instantaneous at −78° in toluene solution. We have confirmed this observation. When *solutions* of NBS in methylene chloride were treated with gaseous HBS at −78°, a bromine color appeared immediately and did not intensify upon standing. Rapid removal of the volatiles *in vacuo* yields a residue of pure succinimide. Since HBr would be pumped off before bromine, this observation indicates reaction 4 goes to completion; k_{eq} is large.

Suspensions of NBS at low temperature react sluggishly with hydrogen bromide at −78°. The reactions of hydrogen bromide with suspensions of *N*-bromosuccinimide in a Freon solvent at −78° are characterized by formation of a yellow-orange precipitate. The ingredients required for formation of the precipitate appear to be molecular bromine, succinimide, and hydrogen bromide. From homogeneous solutions of succinimide and hydrogen bromine or succinimide and bromine in methylene chloride, succinimide is recovered unchanged. But when gaseous hydrogen bromide is bubbled into a methylene chloride solution of

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(10) P. S. Skell, *Chem. Soc., Spec. Publ.*, No. **19**, 131 (1964).

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(12) A report that the unusually high yield of 1,2-dibromobutane from the photobromination of 1-bromobutane may indeed be due to HBr inhibition[13] has not been substantiated.[14,15]

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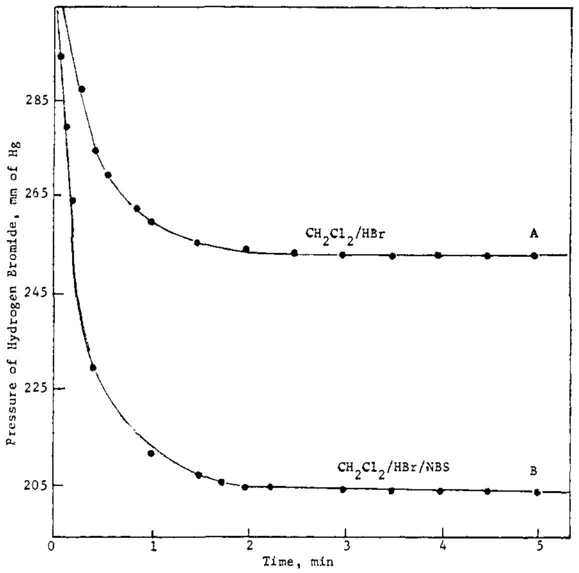


Figure 1. Rate of uptake of hydrogen bromide in methylene chloride and methylene chloride solutions of *N*-bromosuccinimide at 0°.

succinimide and bromine, a yellow-red precipitate forms immediately. The color of the precipitate varies in intensity depending upon the initial bromine concentration. The precipitate is slightly soluble in methylene chloride and readily liberates bromine when *N*-bromosuccinimide is added to the suspension. The complex was shown by titration to contain up to 1 equiv each of HBr and Br_2 depending upon the conditions by which it was generated. Pumping at 10^{-3} mm results in loss of HBr and Br_2, leaving a residue of succinimide. This solid appears to be a molecular complex of composition succinimide–HBr–Br_2.

At temperatures greater than −30°, however, the reaction of NBS with HBr is rapid and complete. The rate of uptake of hydrogen bromide at 0° by stirred suspensions of NBS in methylene chloride and by methylene chloride alone are compared in Figure 1. The equilibrium pressure is reached for both systems in the same time; therefore the rate of reaction of NBS with HBr is as fast as the rate of solution of hydrogen bromide. Further, when the volatiles are rapidly pumped from the NBS system immediately after equilibrium, only a succinimide residue remains. Thus, the reaction under these conditions is rapid and complete.

Bromostasis was demonstrated quantitatively by following spectrophotometrically the concentration of bromine as a bromination progressed. The observations are summarized in Figure 2 in which it is evident that the concentration of bromine remains constant for 85% of the reaction. The individual points were obtained by removing aliquots from the light source and placing it in a preset spectrophotometer; the delay between removal from the light source and making a reading on the spectrophotometer was approximately 5–10 sec. The aliquots were then treated with KI and titrated with thiosulfate.

In poor solvents for NBS at temperatures below −30° caution must be observed to ensure bromostasis since the coating of the unreacted NBS by the relatively insoluble complex occurs more readily. At low

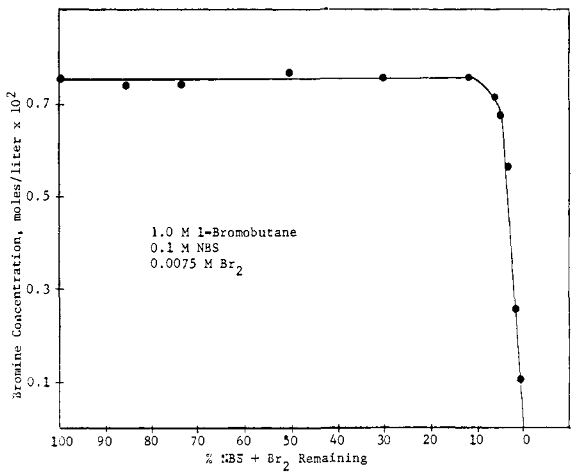


Figure 2. Concentration of bromine during the photobromination of 1-bromobutane in the presence of NBS.

temperatures in perhalocarbon solvents the development of an orange color on the surface of the NBS occurs early, often followed by loss of all color in the supernatant as the photobromination progresses; the utilization of Br_2 outstrips the rate of solution of the NBS. On the other hand, at temperatures above −30°, it is possible to carry out bromostatic photobrominations without this complication, provided good stirring is employed and the rate of reaction is not too large. Following the color of the suspended solid is a recommended precaution.

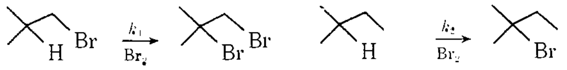
Formation of the molecular complex is not expected to complicate photobromination results. In addition to succinimide and molecular bromine, hydrogen bromide is necessary for its formation. As long as NBS is present in solution, hydrogen bromide is removed immediately; only after the NBS is exhausted are the conditions proper for formation of the complex.

In methylene chloride the formation of a precipitate is a convenient indicator of the progress of a bromination. If one starts with a solution of bromine, substrate and enough NBS to exceed its solubility, as the reaction progresses the remaining NBS goes into solution. Qualitatively it is readily seen that the bromine color remains constant until the precipitate of complex suddenly appears; this is an indication that HBr is beginning to accumulate. If bromostasis is the objective, the appearance of this precipitate can be used to indicate its termination.

Competition Photobrominations

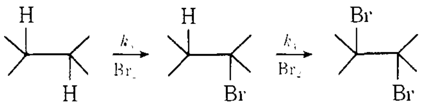
The methylene chloride–bromine–*N*-bromosuccinimide photobromination system was utilized to study a series of intermolecular competitions to assess the influence of halogen substituents on the rates of hydrogen abstraction by bromine atoms.

Isobutyl Bromide–Isopentane. Isobutyl bromide and isopentane are cleanly photobrominated to 1,2-dibromo-2-methylpropane and *tert*-amyl bromide, respectively; substitution occurs exclusively at the tertiary hydrogens.



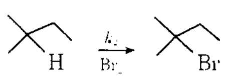
Direct competition of the alkane–alkyl bromide pair, monitoring disappearance of starting material by glc, yields a relative rate ratio $k_1/k_2 = 8.0 \pm 0.5$.

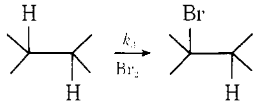
Isobutyl Bromide–2,3-Dimethylbutane. The only product observed from the photobromination of 2,3-dimethylbutane is 2,3-dibromo-2,3-dimethylbutane. In this consecutive bimolecular photobromination, the second step, k_4, is much faster than the first, k_3.



The complication arising from the second step (k_4) was avoided in the competition of 2,3-dimethylbutane and isobutyl bromide by monitoring the disappearance of starting material by glc. In this manner $k_1/k_3 = 5.75$ and $(k_1/k_3)_{\text{per H}} = 11.5 \pm 0.5$ (20°).

Isopentane–2,3-Dimethylbutane. Dividing k_1/k_2 by $(k_1/k_3)_{\text{per H}}$ gives k_3/k_2, a calculated relative rate of photobromination of 2,3-dimethylbutane *vs.* isopentane, $(k_3/k_2)_{\text{per H}} = 0.69$.

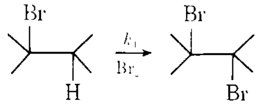


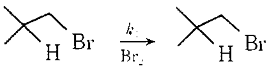


The competition photobromination of isopentane and 2,3-dimethylbutane, monitored by the disappearance of starting material relative to an internal standard, carbon tetrachloride, gave $(k_3/k_2)_{\text{per H}} = 0.65$ (38°). The agreement between the calculated and experimental relative rates provides a measure of the internal consistency.

2-Bromo-2,3-dimethylbutane–2,3-Dimethylbutane. Efforts to calculate k_4/k_3 directly from photobromination of mixtures of 2,3-dimethylbutane and 2-bromo-2,3-dimethylbutane by an nmr method using a published kinetic scheme[19] were unsuccessful. The relative rates were sufficiently different so as to introduce considerable uncertainty in the results. The relative rate constant (k_4/k_3) was calculated indirectly as shown below.

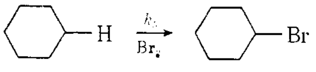
2-Bromo-2,3-dibromobutane–Isobutyl Bromide. This relative rate was calculated from both the decrease in

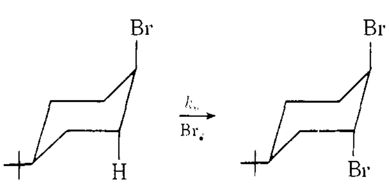




starting materials ($k_4/k_1 = 2.4$) and the appearance of dibromide ($k_4/k_1 = 2.5$) from the nmr peak intensities of the individual bromides. Thus $k_4/k_1 = 2.45 \pm 0.1$. Dividing k_4/k_1 by k_1/k_3 gives $k_4/k_3 = 27.3 \pm 1.7$.

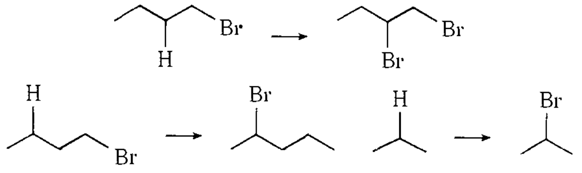
Cyclohexane–*cis*-4-*tert*-Butylcyclohexyl Bromide. The primary photobromination product of cyclohexane is cyclohexyl bromide.[20] The photobromination of *cis*-4-*tert*-butylcyclohexyl bromide had been studied previously.[8] A single product, *trans*-1,2-dibromo-*cis*-4-*tert*-butylcyclohexane, was obtained. The relative rate





constant was obtained by following the reaction products: $k_6/k_5 = 19.2$ (30°). Since there are only two reactive hydrogens on *cis*-4-*tert*-butylcyclohexyl bromide and 12 on cyclohexane,[21] the statistical factor is $12/2 = 6$. Therefore, $(k_6/k_5)_{\text{per H}} = 19.2 \times 6 = 115 \pm 5$.

1-Bromobutane–Propane. Relative reactivities of the β and γ positions of 1-bromobutane *vs.* the secondary position of propane were determined by direct competition studies.



Photobromination of propane yields a single product, 2-bromopropane, under the reaction conditions.[22] The relative rates of hydrogen abstraction were obtained by comparing the yields of 1,2- and 1,3-dibromobutane with 2-bromopropane by glc. The results thus obtained are given in Table I.

1-Chlorobutane–Propane. Bromination of 1-chlorobutane gives 1-bromo-1-chlorobutane, 1-chloro-2-bromobutane, and 1-chloro-3-bromobutane.[2] The relative rates of reaction at the β and γ positions of 1-chlorobutane *vs.* propane were obtained from the yields of β- and γ-bromine substituted 1-chlorobutane and from 2-bromopropane. The results are shown in Table I.

Isobutyl Bromide–Isobutyl Chloride. The photobromination of isobutyl bromide has been discussed previously. Isobutyl chloride is cleanly photobrominated to 1-chloro-2-bromo-2-methylpropane. Pairs of these halides were permitted to compete for a deficiency of

bromine (Br_2 + NBS), determining the product ratios by glc. The relative rate constants (Table II) do not vary over the range of conversions, 3–40%.

Isobutyl Chloride–Isobutyl Fluoride. Photobromination of isobutyl fluoride gives 95% 1-fluoro-2-bromo-2-methylpropane. Isomeric bromofluorides and di-

bromofluorides make up the remainder of reaction products. The relative rate of reaction was determined as above.

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[19] H. G. Higgins and E. J. Williams, *Aust. J. Sci. Res.*, 5, 572 (1952).

[20] Cyclohexyl bromide is subsequently photobrominated to mainly *trans*-1,2-dibromocyclohexane.[2] However, under the competition conditions, the per cent conversion was low (<2%) and no *trans*-1,2-dibromocyclohexane was observed.

[21] The statistical correction implies equal reactivity of axial and equatorial hydrogens on cyclohexane toward bromine atoms.

[22] Substitution at the primary hydrogen was not observed. Photobromination of 2-bromopropane yields 2,2- and 1,2-dibromopropane in addition to 1,2,2-tribromopropane. However, under the conditions of the photobromination (low conversion), these di- and tribromides were not observed.

Table I. Summary of Intermolecular Competition Photobrominations

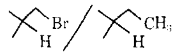
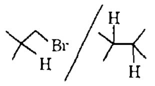
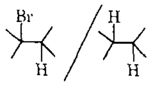
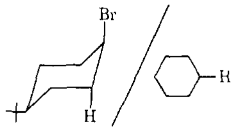
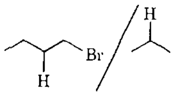
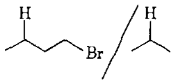
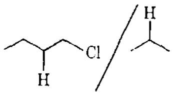
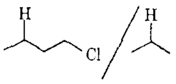
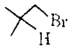
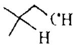
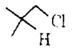
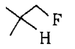
Reactants	Temp, °C	$(k_{RBr}/k_{RH})_{obsd}$	$(k_{RBr}/k_{RH})_{per\ H}$	Anchimeric effect
	30	8.0	8.0	72
	30	5.64	11.3	102
	30		27.3	248
	30	19.2	115	1045
	30	2.87	2.87	26
	30	0.38	0.38	(1.0)
	60	0.092	0.092	(3.0)
	60	0.25	0.25	(1.0)

Table II. Relative Rate of Tertiary Hydrogen Abstraction from Substituted Isobutanes[a]

Compound	k_{rel}
	8.0
	(1.0)
	0.4
	0.036

[a] 20–30°.

Magnitude of Anchimeric Assistance Effect

In each of the competitions studied, hydrogen abstraction β to a bromine substituent was found to be *faster* than in the parent alkane. A chlorine substituent, on the other hand, does not activate β-hydrogen abstraction.

The magnitude of the anchimeric assistance effect can be determined if a value can be estimated for the deactivation to be expected if the β halogen did not assist, that is, if the β-bromine substituent were acting only in a deactivating capacity. The anticipated deactivation was calculated as follows: the γ position of 1-bromobutane is 0.38 times as reactive as propane. As one moves closer to an electronegative substituent, reactivity is expected to decrease. Thus, in the absence of anchimeric assistance the β position would be 0.11 times as reactive as the CH_2 of propane.[23] In fact, the β position of 1-bromobutane is 2.87 times as reactive as propane, indicating the anchimeric effect is 2.87/0.11 = 26. Although this procedure is developed for 1-bromobutane, the same factor is applied to all other systems without making structure corrections. Anchimeric effects are shown in Table I.

The relative rate of hydrogen abstraction from 1-chlorobutane *vs.* propane, on the other hand, exhibits near normal reactivity. At 60° the γ position of 1-chlorobutane is 0.25 times as reactive as propane. Using the same attenuation factor calculated for 1-bromobutane (ϵ 0.38), the calculated reactivity of the β position of 1-chlorobutane is 0.03 times that of propane. The experimental value is 0.09. This small increase in reactivity over the calculated value indicates that a chlorine substituent does not activate the adjacent position.[24]

The failure by Cl or F to supply anchimeric assistance is further illustrated by the photobrominations of the substituted isobutanes (Table II). Only a bromine substituent activates hydrogen abstraction.

Temperature Effects on Relative Reactivity

Alkyl Bromides. The relative rates of bromination of propane and 1-bromobutane at C-3 are insensitive to temperature change. On the other hand, when either of these is compared to the rate of bromination at C-2 there is considerable sensitivity to temperature change. These results are summarized in Table III.

Arrhenius plots are shown in Figure 3 and the differences in activation energies and entropies are summarized in Table IV. The activation energies and en-

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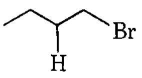
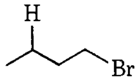
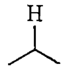
(23) See Appendix.

(24) There is only one report of substantial β-hydrogen activation by chlorine. Traynham and Hines studied the photobromination of 1-chloromethyl-4-methylcyclohexane and found substitution occurred exclusively at the chloromethyl group to give 1-chloromethyl-2-bromo-4-methylcyclohexane.

Table III. Summary of the Temperature Effect on the Relative Rates of Bromination of 1-Bromobutane and Propane[a]


A

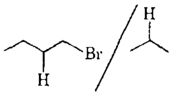
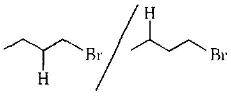
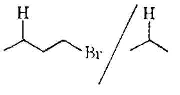

B


C

Temp, °C	k_A/k_C	k_B/k_C	k_A/k_B
60	1.44	0.345	4.06
30	2.87	0.387	7.47
0	4.12	0.345	11.90
−23	7.26	0.319	22.60

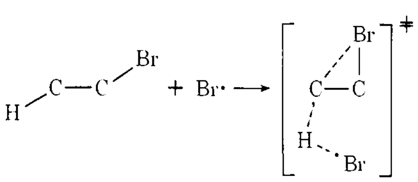
[a] Values are the average of at least two independent runs.

Table IV. Summary of the Activation Energy and Enthalpy Differences from the Competition Photobromination of 1-Bromobutane and Propane

Reactants	ΔE_a, kcal/mol	$\Delta\Delta S^{\ddagger}$, eu
	−3.1	−6.8
	−3.4	−7.2
	0.1	−1.0

tropies are nearly identical for propane and C-3 of 1-bromobutane; at C-2 the activation energy is significantly lower and the activation entropy more negative.

For a variety of unassisted brominations (alkanes) for which differences of activation energies show a range of 10 kcal, all activation entropies fall within a 2-eu range.[25] The considerably more negative entropy of activation at C-2 of 1-bromobutane (7 eu) is indicative of a change in structure of the transition state. The lower activation energy (3 kcal/mol) and the more negative entropy of activation are consistent with the proposed anchimeric assistance scheme for brominations at positions β to a bromo substituent. This results in a weakened C–H bond, and a more ordered transition state characteristic of the loss of rotational freedom in cyclization processes.



Alkyl Chlorides. The results of the competition photobrominations reveal little, if any, activation by a β-chlorine substituent. There is a small temperature dependence of the relative reactivities of β and γ positions in the photobromination of 1-chlorobutane (Table V). The activation energy for hydrogen atom abstraction β to a chlorine atom substituent was calculated to be 400 cal/mol *lower* than γ-hydrogen abstraction. Further, the activation entropy of β-hydrogen abstraction is 2.9 eu more negative than γ-hydrogen abstraction from 1-chlorobutane. The activation energy and entropy differences are much smaller than those for the 1-bromobutane system (3.4 kcal/mol, 7.2 eu), but they are in the same direction. This may be attributed to a weak interaction of the β-chlorine substituent with the incipient radical in the transition state. The β carbon–hydrogen bond is only slightly weakened by this interaction; it appears the unfavorable entropy of activation is controlling. Consequently, bridging in the transition state is not as important as it is in 1-bromobutane. This small anchimeric effect in formation of this β-chloroalkyl radical does not contraindicate the intermediacy of a bridged radical, only that it may be unimportant in describing the transition state for H-abstraction.

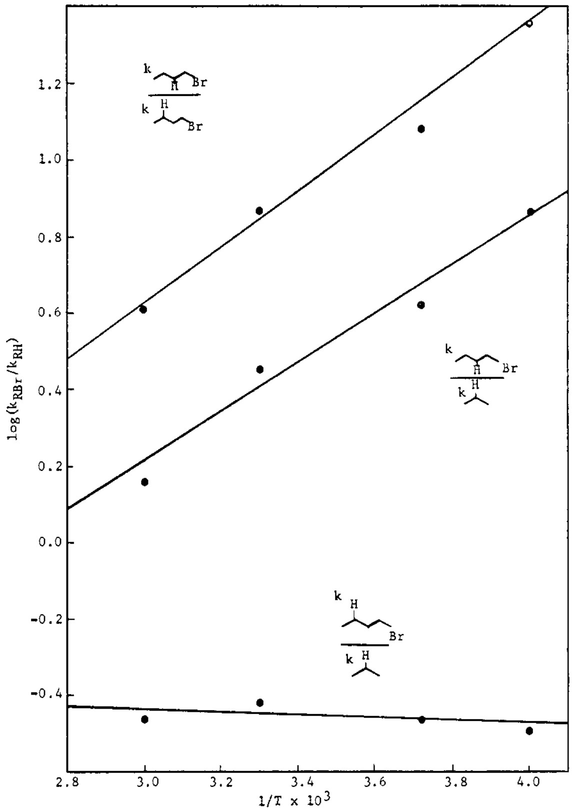
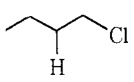
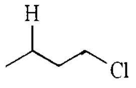
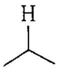


Figure 3. Arrhenius plot of log (k_{RBr}/k_{RH}) *vs.* $1/T$.

Table V. Summary of the Temperature Effects on the Relative Rates of Photobromination of 1-Chlorobutane and Propane[a]


D


E


C

Temp, °C	k_D/k_C	k_E/k_C	k_D/k_E
60	0.092	0.25	0.37
44			0.41
30			0.43
0	0.143	0.28	0.50

[a] Values are the average of at least two independent runs.

Conformational Effects on Reactivity

The relatively small anchimeric assistance effect observed for bromination at C-2 of 1-bromobutane is partially explained by the unfavorable entropy of activation term. If the entropies of activation had been the same at C-2 and C-3, the activation energy effect (3–4 kcal/mol) would have made reaction at C-2 300–400

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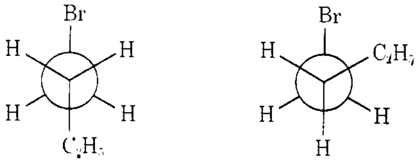
(25) Reference 5, p 151.

times faster than at C-3. Further, since an antiperiplanar configuration has been shown to be a requirement for assistance by a β-bromine substituent,[11e,f,26] it becomes clear that in 1-bromobutane the anchimeric effect is operable only in the less stable conformation. If all factors were favorable, an anchimeric assistance effect of 10^3 might be anticipated.



An effect of this magnitude is observed in the most favorable case of locked cyclohexane; *cis*-4-*tert*-butyl-1-bromocyclohexane has bromine locked in the axial position and the flanking carbons have axial hydrogens, making an antiperiplanar configuration. This compound is brominated to give a single product. It reacts 115 times faster than cyclohexane on a per hydrogen basis. If the deactivating effect of a nonassisting β-bromo substituent is included, an anchimeric effect of 1440 is obtained.

Free-Radical Cage Effects

The calculations of relative rates employed have depended on the assumption that a hydrogen atom once removed by a bromine atom did not return; that is, the products are under kinetic control. The scavenging effect of NBS eliminates the free hydrogen bromide required for the reverse reaction. However, if the geminate pair $R\cdot$ HBr recombined at different rates as R was changed, some uncertainty would be introduced into the interpretation since NBS could not affect this reversal.

First, even when a radical pair is generated in a solvent cage, recombination within the cage usually occurs in less than 50% of the instances.[27,28] Thus, if cage effects did not exceed this value for bromination, the uncertainty in relative rates would not exceed a factor of 2.

Second, there are no reports of evidence that such cage recombinations occur, only a report of a failure to find it in the photobromination of (+)-2-chlorobutane.[11f] In this instance, after more than 50% conversion to $CH_3\dot{C}ClCH_2CH_3$ had taken place, the recovered 2-chlorobutane was less than 3% racemized. It was possible to reason that either there was not return within the cage, or cage return occurred with a rate constant in excess of 10^{11} sec^{-1}. The latter seems unlikely; we are still investigating these possibilities.

Experimental Section

General. Nmr spectra were obtained on Varian A-60-A and HA-100 spectrometers. Chemical shifts are reported on the τ scale, relative to TMS added as internal standard. Glc analyses were performed on Nittany Scientific thermal conductivity or Perkin-Elmer F-11 hydrogen flame instruments. Products were identified by comparison of glc retention times and spectra with those of authentic samples. Visible spectra were recorded with a Spectronic 20 spectrophotometer. Photolyses were carried out with 300-W tungsten filament frosted light bulbs or G E A-H6 high pressure mercury arc (soft glass filter).

Materials. Hydrogen bromide (Matheson) was trap to trap distilled on a vacuum line prior to use. Bromine was distilled through an all glass apparatus. Methylene chloride was purified by successive washes with H_2SO_4, Na_2CO_3 (5%), and $NaHCO_3$ (5%). After drying ($CaCl_2$), the solvent was distilled over P_2O_5 and stored over 4A molecular sieve.

1-Bromobutane (Matheson) was redistilled prior to use. Glc analysis showed the bromide to be pure. *N*-Bromosuccinimide (Aldrich) was used without further purification.

The purity of the alkyl halides and hydrocarbons used in this study was checked by nmr and glc analysis.

1,2-Dibromo-2-methylpropane [nmr (CCl_4) τ 8.12 (s, 6 H), 6.14 (s, 2 H)] and 2,3-dibromo-2,3-dimethylbutane [nmr (CCl_4) τ 7.98 (s)] were prepared by the addition of bromine to isobutylene and tetramethylene, respectively.

2-Bromo-2,3-dimethylbutane was prepared by bubbling gaseous hydrogen bromide into neat 2,3-dimethylbutene. The resulting solution was washed until neutral to litmus, dried (K_2CO_3), and distilled *in vacuo*: bp 49° (83 mm) [(lit[6b] bp 65° (100 mm)]; nmr (CCl_4) τ 8.97 (d, J = 7 Hz, 6 H), 8.27 (s and m, 7 H).

cis-4-*tert*-Butylcyclohexyl bromide was prepared by the method of Eliel and Haber.[29]

Isobutyl fluoride was prepared by the method of Yarovenko and Rahska:[30] nmr (CCl_4) τ 9.08 (d, J = 6.5 Hz, 6 H), 8.1 (m, 1 H), 5.98 (doublet of doublets, J = 6.5 and 48 Hz, 2 H).

1-Chloro-2-bromo-2-methylpropane was the minor product (5%) from the addition of BrCl to isobutylene; nmr (CCl_4) τ 8.19 (s, 6 H), 6.17 (s, 2 H). Other products from this reaction are: 1-bromo-2-chloro-2-methylpropane (90%), nmr τ 8.27 (s, 6 H); and 1,2-dibromo-2-methylpropane (5%), nmr τ 8.13 (s, 6 H), 6.14 (s, 2 H).

Reactions of NBS with Hydrogen Bromide. Gaseous hydrogen bromide was introduced from a vacuum line into stirred solutions of NBS. After various contact times, the volatile materials were pumped from the solution and the residue was treated with KI and analyzed by thiosulfate titrimetry.

For studies of the rate of uptake of hydrogen bromide, a bulb containing hydrogen bromide was attached to a vacuum line. A flask containing the reactants was similarly fitted to the line. The small section of line connecting the two flasks contained a mercury manometer. After degassing by several freeze–thaw cycles and equilibration at 0°, the hydrogen bromide was introduced into the system while the pressure was continuously recorded.

Bromostasis. The bromine concentration was monitored during photobromination of 1-bromobutane. A nitrogen purged solution of bromine (0.0075 *M*), NBS (0.1 *M*), and 1-bromobutane (1 *M*) in methylene chloride was irradiated with a 300-W tungsten filament lamp. Aliquots were removed during the photolysis and rapidly analyzed spectrophotometrically (440 mμ) for bromine concentration (analysis was complete within 5–10 sec). The aliquots were then analyzed for total oxidizing power by iodine thiosulfate titrimetry.

Photobrominations. Isopentane. A 100-ml, three-necked flask (Dry Ice condenser, nitrogen inlet, and magnetic stirrer) was charged with trichlorofluoromethane (16 ml), *N*-bromosuccinimide (2.0 g, 11.2 mmol), isopentane (8 ml, 69 mmol), and bromine (1.1 g, 6.8 mmol). The flask was purged with nitrogen, then maintained at a static atmosphere of nitrogen. The solution was photolyzed with a 60-W frosted tungsten filament lamp (5 in.). Aliquots were removed during the course of the reaction, chilled to −78°, then treated with propylene to discharge the remaining bromine. Analysis by glc (Nittany Scientific, 25% Carbowax 1000 on 60–80 Gas Chrom R, 38°, 138 ml/min) revealed the presence of a single photobromination product during all stages of the reaction (30 min). Removal of solvent and unreacted isopentane, followed by filtration, yielded a pale yellow residue (2.6 g, 94%): nmr (neat) τ 8.98 (t, J = 7 Hz, 3 H), 8.34 (s) and 8.25 (quartet, J = 7 Hz), totaling 8 H. The nmr spectrum was identical with that of an authentic sample of *tert*-amyl bromide.

Isobutyl Bromide. The preliminary photobromination of iso-

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[26] P. S. Skell and K. J. Shea, *Isr. J. Chem.*, **10**, 493 (1972).

[27] (a) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970); (b) O. Dobis, J. M. Pearson, and M. Szuarc, *ibid.*, **90**, 278 (1968); (c) T. Koenig and H. Fischer in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, p 157.

[28] In solvents of unusually high viscosity or in solid matrices the fraction of cage recombination is much higher; see, for example, H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 667 (1967).

[29] E. L. Eliel and R. G. Haber, *J. Org. Chem.*, 24, 143 (1959).

[30] N. N. Yarovenko and M. A. Rahska, *Zh. Obshch. Khim.*, **29**, 2159 (1959); *Chem. Abstr.*, **54**, 9724 (1960).

butyl bromide was run without NBS present. Subsequent competitions were run in the NBS–Br_2 system. Isobutyl bromide (5.0 g, 36.5 mmol) and methylene chloride (25 ml) were placed in a 100-ml flask equipped with a nitrogen inlet, cold water condenser, and dropping funnel. The flask was purged with nitrogen, then maintained at a static nitrogen atmosphere. Bromine (2.91 g, 18.2 mmol) was added dropwise to the flask while illumination was provided by a 300-W tungsten filament lamp (7 in.). After a brief induction period, the bromine color was rapidly discharged. Bromine was then added at such a rate so as to maintain a pale color at all times. The time of addition was approximately 0.5 hr. A sample of this reaction solution was injected for glc analysis (Nittany-Scientific, Carbowax 1000, 60°). A single product peak was detected. The reaction mixture was washed with dilute sodium bisulfite and water, then dried over anhydrous potassium carbonate. Distillation under reduced pressure afforded 2.9 g (73%) of a colorless liquid: bp 67–70° (60 mm); nmr (CCl_4) τ 8.14 (s, 6 H), 6.14 (s, 2 H). The product had an identical nmr with a sample of 1,2-dibromo-2-methylpropane, prepared by the addition of bromine to isobutylene.

Isobutyl Chloride. A stirred, degassed solution of bromine (9.0 mmol), *N*-bromosuccinimide (6.4 mmol), and isobutyl chloride (4.6 mmol) in trichlorofluoromethane was irradiated for 2.1 hr with a 500-W tungsten filament bulb. The reaction mixture was filtered, then solvent and unreacted bromine were removed by codistillation, affording a residue (0.67 g, 85%) of 1-chloro-2-bromo-2-methylpropane: nmr (CCl_4) τ 8.19 (s, 6 H), 6.17 (s, 2 H). The glc retention time and nmr spectra are identical with the minor product of the BrCl addition to isobutylene.

Isobutyl Fluoride. A nitrogen-purged, stirred solution of *N*-bromosuccinimide (6.2 mmol), bromine (9.0 mmol), and glc purified isobutyl fluoride (6.8 mmol) in trichlorofluoromethane (5 ml) was irradiated with a 500-W tungsten filament bulb (8 in.) at 15° for 15 hr. After filtration of solids and removal of solvent and unreacted bromine, the nmr spectrum of the residue (0.27 g) indicated 1-fluoro-2-bromo-2-methylpropane [(τ 8.21 (d, J = 1.4 Hz, 6 H), 5.62 (d, J = 47.8 Hz, 2 H)] was the major product (>90%) from the reaction. Additional minor absorptions were observed at τ 8.12, 8.00, 6.14, and 5.44 (d, 47 Hz). Glc analysis of the residue (15 ft × 0.25 in. Carbowax 1000, 55°) showed the major product with a retention time of 13 min (92%); a broad peak (8%) with a retention time of 88 min was the only other product observed. This higher boiling product is tentatively assigned to a dibromofluorobutane.

The duration of the photobromination was long compared with the competition photobrominations studied. During these shorter reactions, considerably smaller yields of higher boiling materials were observed.

2,4-Dimethylbutane. A 50-ml flask, fitted with a mechanical stirrer, condenser, and nitrogen inlet, was charged with 15 ml of methylene chloride, 2,3-dimethylbutane (7.55 g, 87.8 mmol), and *N*-bromosuccinimide (4.0 g, 22.5 mmol). The stirred solution was cooled to 0° and purged with nitrogen. A nitrogen atmosphere was maintained for the duration of the reaction. Bromine (0.8 mmol) was added to the flask and the reaction mixture was irradiated with a 60-W tungsten filament lamp (4 in.) for 45 min. The volume of the reaction mixture was reduced and an nmr of this crude reaction mixture indicated a single product, 2,3-dibromo-2,3-dimethylbutane [τ 7.98 (s)], was present. No peak corresponding to 2-bromo-2,3-dimethylbutane was detected (τ 8.27 and 8.97) in the nmr. The residue was filtered to remove succinimide (2.3 g, 98%, mp 122°) and final traces of solvent were removed on the rotary evaporator yielding 2.3 g (82%) of 2,3-dibromo-2,3-dimethylbutane; nmr (CCl_4) τ 7.98 (s).

Utilizing the procedure described above, a number of attempts were made to determine if 2-bromo-2,3-dimethylbutane was a reaction product during the initial stages of the photobromination. Aliquots of the reaction mixture were removed at various times during the photolysis and cooled to −78°. Bromine was quenched by bubbling propylene into the aliquot and the samples were quickly analyzed by nmr. At no time during the photolysis was 2-bromo-2,3-dimethylbutane detected as a reaction product; only 2,3-dibromo-2,3-dimethylbutane was observed.

Competition Photobrominations. Isobutyl Fluoride–Isobutyl Chloride. A stirred, degassed solution of *N*-bromosuccinimide (12.0 mmol), bromine (18.0 mmol), isobutyl chloride (4.7 mmol), and isobutyl fluoride (4.7 mmol) in trichlorofluoromethane (10 ml) was irradiated at 14° with a 500-W bulb. Aliquots were removed at various times during the photolysis, chilled to 0°, treated with pentene to destroy the excess bromine, and analyzed directly by glc. The molar ratios of 1-fluoro-2-bromo-2-methylpropane were used to calculate the relative rate of photobromination. The relative rate, from 15 to 65 min photolyses (0.5–2.13% conversion of isobutyl fluoride and 20–74% conversions of isobutyl chloride), was 11.0 ± 1.0.

Isobutyl Chloride–Isobutyl Bromide. A stirred, degassed solution of *N*-bromosuccinimide (12 mmol), bromine (18 mmol), isobutyl bromide (4.6 mmol), and isobutyl chloride (4.7 mmol) in trichlorofluoromethane (10 ml) was irradiated at 15° (500-W tungsten filament). Aliquots were removed and quenched with olefin, then analyzed by glc. The molar ratios of isobutyl chloride, isobutyl bromide, and 1-chloro-2-bromo-2-methylpropane were used to calculate the relative rate constant as in the previous competition. Between 1 and 7 min of photolysis (2.6–15% conversion of isobutyl bromide), $k_{\text{isobutyl bromide}}/k_{\text{isobutyl chloride}} = 20 \pm 1.0$.

Isopentane–Isobutyl Bromide. The relative rate of tertiary hydrogen abstraction from isopentane and isobutyl bromide was determined by disappearance of starting materials relative to an internal standard, carbon tetrachloride.

A solution containing approximately 25 mmol each of isobutyl bromide, isopentane, and carbon tetrachloride was diluted to 25 ml with methylene chloride. The initial ratio of reactants to internal standard, CCl_4, was determined by glc. The solution was transferred to a 50-ml flask containing *N*-bromosuccinimide (13.6 mmol). After purging with nitrogen for 60 sec, 1.0 mmol of Br_2 was introduced into the flask. Stirring was commenced and the solution was irradiated with the A-H6 lamp for 5.0 min. Analysis by glc was performed to determine the final ratio of reactants relative to carbon tetrachloride. Using the following relative rate relationship, the relative rate was calculated using the expression

$$\frac{k_{\text{isobutyl bromide}}}{k_{\text{isobutane}}} = \frac{\log \dfrac{([\text{isobutyl bromide}]/[CCl_4])_{\text{final}}}{([\text{isobutyl bromide}]/[CCl_4])_{\text{initial}}}}{\log \dfrac{([\text{isobutane}]/[CCl_4])]_{\text{final}}}{([\text{isobutane}]/[CCl_4])_{\text{initial}}}}$$

The photolysis converted 9.8% isobutane and 43% isobutyl bromide to product and $k_{\text{isobutyl bromide}}/k_{\text{isobutane}} = 8.0 \pm 0.5$.

Isobutyl Bromide–2,3-Dimethylbutane. A solution of isobutyl bromide (25 mmol), 2,3-dimethylbutane (27 mmol), and carbon tetrachloride (26 mmol) was analyzed by glc to obtain the initial ratio of reactants to internal standard (CCl_4). Bromine (1.0 mmol) and *N*-bromosuccinimide (14 mmol) were added, and the solutions were purged with nitrogen, then irradiated with stirring at 30°, with the A-H6 lamp for 5 min (at this time the bromine color began to diminish). The final ratios of reactants were determined relative to standard (CCl_4) by glc: 56.1% of isobutyl bromide and 9.6% of 2,3-dimethylbutane had reacted. Calculation of the relative rate constant, as in the preceding experiment,gave $k_{\text{isobutyl bromide}}/k_{\text{2,3-dimethylbutane}} = 5.6 \pm 0.5$.

Isobutyl Bromide–2-Bromo-2,3-dimethylbutane. Quantitative nmr was employed to monitor the disappearance of starting bromides relative to an internal standard, benzene.

A solution of 2-bromo-2,3-dimethylbutane (10 mmol), isobutyl bromide (9.80 mmol), and benzene (8.58 mmol) was weighed and diluted to 10.0 ml with methyl chloride. An aliquot was removed for nmr analysis to obtain the peak area ratios of benzene (τ 7.63) to isobutyl bromide (τ 6.81 (d)) and 2-bromo-2,3-dimethylbutane (τ 8.93). The solution was transferred to the photolysis tube containing a magnetic stirring bar and *N*-bromosuccinimide (5.39 mmol). After purging with nitrogen, bromine (0.06 mmol) was added and the solution was photolyzed (vigorous stirring maintained) until the disappearance of bromine color (2 min). The final ratios of reactants to the internal standard were then recorded by nmr. Under these conditions 57% of 2-bromo-2,3-dimethylbutane and 44% of isobutyl bromide reacted. Thus, $k_{\text{2-bromo-2,3-dimethylbutane}}/k_{\text{isobutyl bromide}} = 2.4$.

The ratio obtained when the relative rate is calculated using initial ratio of reactants and the final ratio of products 2,3-dibromo-2,3-dimethylbutane (τ 7.98) and 1,2-dibromo-2-methylpropane (τ 6.78) is 2.5.

A control reaction was run in the absence of light. The bromine was discharged with propylene after 3 min. The ratios of reactants to internal standard (benzene) remained unchanged (±2%).

***cis*-4-*tert*-Butylcyclohexane–Cyclohexane.** A reaction tube, fitted with a magnetic stirring bar, was charged with *N*-bromosuccinimide (0.534 g, 3.0 mmol), *cis*-4-bromo-*tert*-butylcyclohexane (1.35 g, 6.16 mmol), cyclohexane (3.15 g, 37.5 mmol), and 15 ml of a bromine–methylene chloride (0.45 mmol of Br_2) solution. The tube was foil wrapped, degassed by several freeze–thaw cycles, then equilibrated at 30° in a constant-temperature bath in the dark for 10 min. The homogeneous solution was photolyzed with a 300-W tungsten filament lamp (10 cm) for 11 min. The bromine color still persisted; the reaction did not go to completion. The remaining bromine was discharged with a small amount of corn oil. Analysis by glc revealed, in addition to the two starting materials, two new products: cyclohexyl bromide (0.55 mmol) and *cis*-4-*tert*-butyl-*trans*-1,2-dibromocyclohexane (1.83 mmol). The relative rate was calculated from the expression

$$\frac{k_{cis\text{-4-}t\text{-butylcyclohexyl bomide}}}{k_{\text{cyclohexane}}} = \left(\frac{\text{mmol of cyclohexane}}{\text{mmol of } cis\text{-4-}t\text{-butylcyclohexyl bromide}}\right)_{\text{initial}} \times \left(\frac{\text{mmol of } cis\text{-4-}t\text{-butylcyclohexyl bromide product}}{\text{mmol of cyclohexane product}}\right)_{\text{final}}$$

Thus, $k_{\text{RBr}}/k_{\text{RH}} = 20.1$. In a duplicate reaction, $k_{\text{RBr}}/k_{\text{RH}} = 18.6$.

1-Halobutane–Propane. Propane (25 mmol) was condensed from a vacuum line into a foil wrapped 15-ml pressure tube (Fisher-Porter valve) containing a degassed solution of 1-halobutane (2.5 mmol), *N*-bromosuccinimide (2.0 mmol), and methylene chloride (12 ml). The reaction tube contained a small magnetic stirring bar. After equilibration in a constant-temperature bath for 10 min with vigorous stirring, the foil was removed and the stirred solution was irradiated with a 300-W tungsten filament lamp (3 in.) for a length of time so as to affect only partial conversion (20–130 min). Propylene was condensed into the tube to destroy the bromine. 1,3-Dibromopropane was added as an internal standard and the reaction mixture was analyzed directly by glc. The relative rate constants, the average of at least two independent runs, were calculated from the initial ratio of starting materials and final product ratios. For example

$$\frac{k_{\text{1,2-dibromobutane}}}{k_{\text{propane}}} = \left(\frac{\text{mmol of propane}}{\text{mmol of 1-bromobutane}}\right)_{\text{initial}} \times \left(\frac{\text{mmol of 1,2-dibromobutane}}{\text{mmol of 2-bromopropane}}\right)_{\text{final}}$$

Isopentane–2,3-Dimethylbutane. A 100-ml flask, fitted with a magnetic stirrer, Dry Ice–acetone condenser, and nitrogen inlet, was charged with 10.2 g of *N*-bromosuccinimide (57.4 mmol) and 20 ml each of isopentane and 2,3-dimethylbutane (*ca.* 0.2 mmol). Carbon tetrachloride (16 ml, 0.16 mmol) was added as the internal standard. The flask was purged with nitrogen, then maintained at a static nitrogen atmosphere. Bromine (0.13 ml, 2.5 mmol) was added and the solution was photolyzed with a 300-W tungsten filament lamp (5 in.). The bromine color started to dissipate after 2.5 hr of photolysis. The flask was stoppered and samples of the reaction mixture and original solution were injected for glc analysis; 12.3% of isopentane and 15.5% of 2,3-dimethylbutane had reacted at this time. The rate expression used above was employed; thus, $k_{\text{isopentane}}/k_{\text{2,3-dimethylbutane}} = 0.78$.

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Appendix

Estimation of Anchimeric Effects. It is possible to obtain a rough estimate of the reactivity of aliphatic compounds containing a single polar group by assuming the inductive effect falls off by a constant factor, ϵ, per methylene group. Two methods were used to calculate the reactivity of the β position of 1-bromobutane relative to a secondary alkane.

Using a method employed by Peterson, *et al.*,[31] an attenuation factor, ϵ, was calculated for a bromine substituent from the relative rate of γ- and δ-hydrogen abstraction by bromine atoms from 1-bromoheptane;[32] $\delta/\gamma = 1.64$. Further, the γ position of 1-bromobutane is 0.38 times as reactive as a secondary alkane (propane). Thus

$$\log (k_{\text{alkane}}/k_{\gamma}) = \epsilon^{\gamma-\delta} \log (k_{\text{alkane}}/k_{\delta})$$

$$\log 1/0.38 = \epsilon \log 1/1.64 \times 0.38$$

$$\epsilon = 0.48$$

To obtain the reactivity at the β position of 1-bromobutane

$$\log (k_{\text{alkane}}/k_{\gamma}) = 0.48 \log (k_{\text{alkane}}/k_{\beta})$$

$$k_{\beta} = 0.13$$

A second calculation employed the Taft $\sigma\rho$ equation. The σ^* values for a series of bromoalkyl groups were estimated as follows:[33] CH_2Br, 1.00; CH_2CH_2Br, 0.36; $CH_2CH_2CH_2Br$, 0.13. Using the above δ^* constants and the relative reactivities of γ and δ positions of 1-bromoheptane, a ρ for aliphatic free radical bromination is calculated

$$\log (k_{\text{alkane}}/k_{\gamma\text{position}}) = \sigma_{\gamma}\rho$$

$$\log (k_{\text{alkane}}/k_{\delta\text{position}}) = \sigma_{\delta}\rho$$

substracting, $\log (k_{\delta}/k_{\gamma}) = (\delta_{\gamma} - \sigma_{\delta})\rho$; thus, $\rho = -0.93$. Using $\rho = -0.93$, the reactivity of the β position of 1-bromoalkane is calculated by

$$\log (k_{\text{alkane}}/k_{\gamma}) = \rho\sigma_{\gamma}$$

$$\log (k_{\text{alkane}}/k_{\beta}) = \rho\sigma_{\beta}$$

$$\log k_{\gamma}/k_{\beta} = (-0.93)(\sigma_{\gamma} - \sigma_{\beta})$$

Therefore $k_{\gamma}/k_{\beta} = 3.94$. Since k_{γ} is 0.35 times as reactive as a secondary hydrogen, $k_{\gamma} = (0.35)(1/3.94) = 0.09$.

The average value of 0.11 was taken to indicate the estimated relative reactivity of a hydrogen β to a bromine substituent if the bromine were acting only in a deactivating capacity.

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