

The Mechanism Study of Free Radical S_H2' Reactions by Leaving Group Effect and Secondary α -Deuterium Kinetic Isotope Effect

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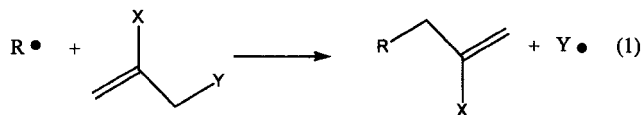
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The reactions of free radical addition to allylic compounds are believed to proceed the S_H2' mechanism. It is not clear whether the S_H2' mechanism is concerted or stepwise. The leaving group effects and the secondary α -deuterium kinetic isotope effects in free radical S_H2' reactions have been determined. The leaving group effect, k_{Br}/k_{Cl} , is from 1.88 to 14.3. The secondary α -deuterium kinetic isotope effects, k_H/k_D , are 1.20 for 2-methylallyl chloride and 1,1-d₂-2-methylallyl chloride and 1.22 for allyl chloride and 1,1-d₂-allyl chloride. The free radical S_H2' reactions seem to favor the concerted mechanism.

Keywords: Solvent effect; Free radical S_H2' reaction; Isotope effects; *tert*-Butyl radical addition; Concerted mechanism; Stepwise mechanism.

INTRODUCTION

The reactions of free radical addition to allylic compounds have been investigated for more than two decades. The formation of a new carbon-carbon single bond by an S_H2' mechanism involving the attack of a carbon radical onto a double bond by displacement of a radical from the allylic position is a useful synthetic process (eq 1).



The Kosugi group,¹ Grignon group,² and Keck group,³ using allyltributylstannane, developed a method for the allylation of halides and pseudohalides. Schroer and Neumann⁴ indicated that phenyl or *tert*-butyl radical added to 3-tributylstannyl cyclopentene to proceed the S_H2- γ mechanism to form 3-phenyl cyclopentene or 3-*tert*-butyl cyclopentene. Barton and Crich indicated⁵ that there are two possible mechanisms for the S_H2' process: first, one in which the addition of the radical is concerted with the loss of the leaving radical (Scheme I, path a); second, a stepwise mechanism in which the adduct radical has a definite existence (Scheme I, path b).

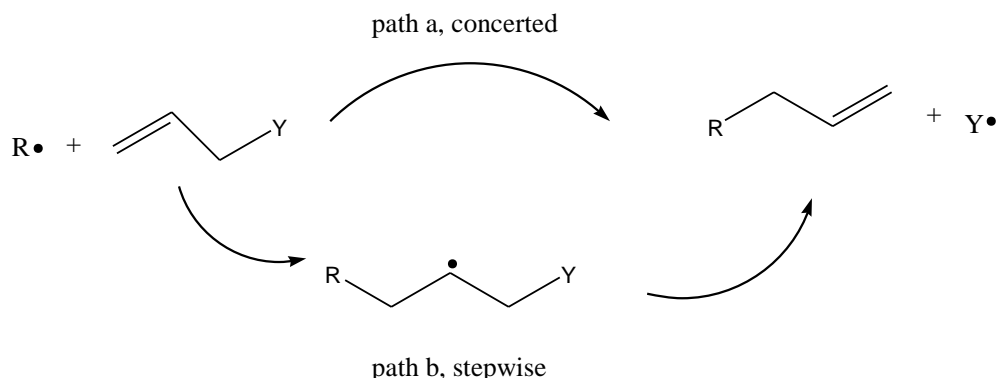
The Migita group reported that the reactions of phenyl radical with allylic sulfides and halides yielded allyl benzene

as a major product, and the stepwise mechanism was proposed to explain the reactions.⁶ However, a concerted S_H2' mechanism was suggested by Barton and Crich for the reaction of alkyl radical with allylic derivatives.⁵ Russell et al.⁷ indicated that the *tert*-butyl radical addition to allyl derivatives proceeded with the stepwise S_H2' reaction mechanism, and the radical addition to double bond is a rate-determining step. Therefore, the controversy that exists in the S_H2' mechanism of the free radical addition reaction still remains to be elucidated.

In our previous report,⁸ we studied the substituent effects of the *tert*-butyl radical addition to 2-substituted allyl chlorides (eq 1) with substituents (X) including H, CH₃, CH₂Cl, CH₂OPh, CH₂SiMe₃. The correlation of log k/k_0 vs. σ_m gave a ρ value of 3.59 with a correlation coefficient of 0.930. However, when the substituent CH₂Cl was excluded, the correlation coefficient rose to 0.990 and the ρ value became 3.39. The substituent effect indicates that the radical addition to double bond is the rate-determining step in the S_H2' reaction, which is consistent with the mechanism proposed by Russell.⁷ However, it is hard to explain why the substituent CH₂Cl has a large deviation in the substituent effects of S_H2' reactions. The electronic and steric effects should not be responsible for the deviation of substituent CH₂Cl in the *tert*-butyl radical addition reactions.⁸ We could not rationalize the deviation of substituent CH₂Cl unless

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Scheme I



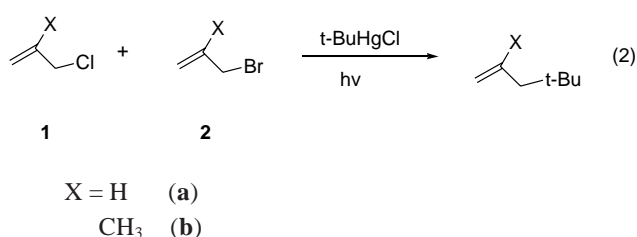
there are two leaving groups in this molecule. If the reaction rate could be alternated by the number of leaving groups, we might guess the rate-determining step of the S_H2' reaction should involve the rupture of the leaving group. Therefore, one of the possibilities for the deviation of substituent CH_2Cl might be that the reaction of the free radical addition to allyl chloride did not proceed with the stepwise mechanism as Russell proposed. This leads us to investigate the mechanism of the S_H2' reaction.

In this article, we use the leaving group effect and the secondary α -deuterium kinetic isotope effect to clarify the mechanism of the radical S_H2' reaction.

RESULTS AND DISCUSSION

The leaving group effects in free radical S_H2' reactions

Bunnett et al.⁹ introduced the use of the element effect in the study of nucleophilic aromatic substitution. A comparative study of the reactivity of aryl chlorides and bromides resulted in the k_{Br}/k_{Cl} ratio being close to unity. Based on the assumption that the electronic effect of Cl and Br were similar, this observation provided strong evidence for the intermediacy of the stepwise mechanism. However, if the k_{Br}/k_{Cl} ratio was greater than unity, then the reaction might encourage the concerted mechanism. Thus, we try to use the element effect to investigate the free radical S_H2' reaction mechanism. The competitive kinetic experiments were carried out by a pair of 2-substituted allyl chloride or bromide (at least 10 times with respect to t -BuHgCl in Me_2SO) under photolysis. It is difficult to determine the leaving group effect directly from the following competitive reactions (eq 2), because the same product was obtained from the photolytic reaction of the 2-substituted allyl chloride and 2-substituted allyl bromide with t -BuHgCl.



Then, the leaving group effects were determined indirectly by the following method. The relative rates of the following pairs, 2-methylallyl chloride (**1b**) and allyl chloride (**1a**), compound **1b** and allyl bromide (**2a**), 2-methylallyl bromide (**2b**) and compound **1a**, were determined by the relative amounts of two adducts by GC. Identification of substitution products was confirmed by comparison of their GCMS data with those of the authentic compounds synthesized by methods reported in the literature.⁸ The relative rate ratios are shown in Table 1.

The k_{1b}/k_{1a} , k_{1b}/k_{2a} and k_{2b}/k_{1a} are 0.75, 0.40 and 2.45 respectively. The k_{Br}/k_{Cl} ratios of the leaving group effects, k_{2a}/k_{1a} and k_{2b}/k_{1b} , are determined indirectly by simple calculation and the results are shown in Table 2.

The k_{Br}/k_{Cl} ratio is 1.88 (k_{2a}/k_{1a}) for compounds **2a** and **1a**, and is 3.26 (k_{2b}/k_{1b}) for compounds **2b** and **1b**. The k_{Br}/k_{Cl} ratios of the leaving group effect of 2-substitutedallyl halides all are greater than unity and seem dependent upon the substituent X. This implies that the free radical S_H2' reaction might prefer the concerted mechanism.

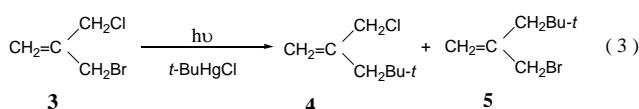
Giese¹⁰ has reported that the rates of alkyl radicals addition to alkenes are controlled mainly by the polar effects of the substituents. Therefore, the substituent effects of the free radical addition reactions must be the same for different leaving groups, if the leaving group effects would be determined properly. In our previous work,¹¹ we investigated the leaving group effect of free radical S_H2' reaction by another method.

Table 1. Relative rates in the addition reactions of *t*-butyl radical to substrates X and Y in DMSO

Substrate X	Substrate Y	Conditions ^a	k _X /k _Y
1b	1a	hν 3 h in DMSO	0.75
1b	2a	hν 3 h in DMSO	0.40
2b	1a	hν 3 h in DMSO	2.45
1b	7	hν 3 h in DMSO	0.92
1a	8	hν 3 h in DMSO	1.60

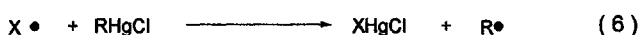
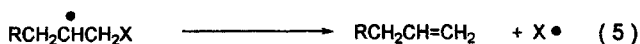
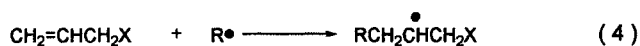
^a The mixture in a 5 mm quartz tube was irradiated at 30–40 °C with a 100 W UV lamp ca. 20 cm from the tube. Each reaction was run at least three times. Error was ± 4%.

The 2-bromomethyl-3-chloro-1-propene (**3**) includes two different leaving groups, Cl and Br; the substituent effect would be identical for these two leaving groups in S_H2' reaction (eq 3). The relative β-elimination rate of the leaving group, k_{Br}/k_{Cl}, can be determined from the yield ratio of products **4** and **5**. The k_{Br}/k_{Cl} ratio of the leaving group is 14.3 which was determined experimentally in CH₃CN.



In order to distinguish these two different kinds of leaving groups, the leaving group effect of eq 2 is named as “the intermolecular leaving group effect” and the leaving group effect of eq 3 is named as “the intramolecular leaving group effect”. Russell et al.⁷ indicated that the *tert*-butyl radical addition to allyl derivatives proceeded with the S_H2' reaction mechanism as shown in Scheme II.

Scheme II



The alkyl radical adds to the terminal carbon of the double bond to form an intermediate radical, which undergoes fast β-elimination of the leaving group X• in a chain process. If the S_H2' reactions would obey the mechanism as Russell proposed, the photolysis of the compound **3** with *t*-BuHgCl should have rendered the mechanism as shown in Scheme III.

The radical **6** should have been generated by addition of *t*-butyl radical to the alkene **3**. These fragments in an intramolecular competition reaction would give the products **4**

Table 2. The intermolecular leaving group effects of 2-substituted allyl halides in the S_H2' reactions

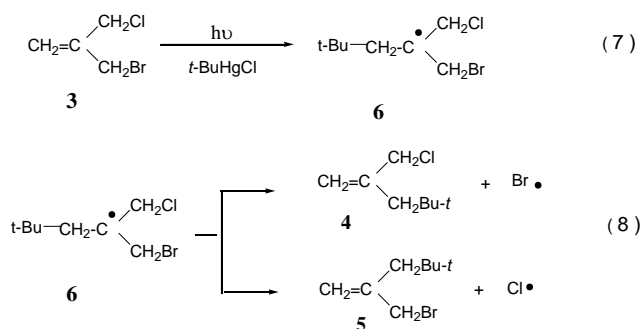
Substrate Br	Substrate Cl	k _{Br} /k _{Cl}
2a	1a	1.88 ^a
2b	1b	3.26 ^b

^a k_{2a}/k_{1a} = k_{1b}/k_{1a} ÷ k_{1b}/k_{2a}

^b k_{2b}/k_{1b} = k_{2b}/k_{1a} ÷ k_{1b}/k_{1a}

k_{1b}/k_{1a}, k_{1b}/k_{2a} and k_{2b}/k_{1a} were cited from Table 1.

Scheme III

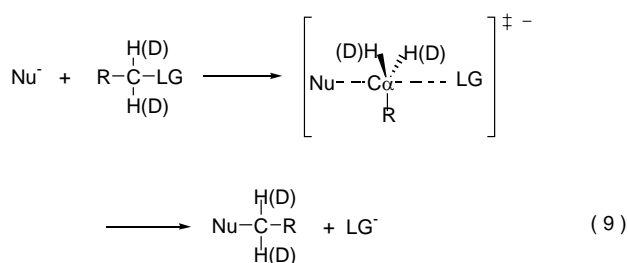


and **5** with cleavage of bromo and chloro radicals, respectively. The value of k_{Br}/k_{Cl} should be dependent upon the amount of ΔΔG[‡], which is the free activation energy difference between the reactions of the rupture of bromo radical and chloro radical from the adduct radical **6**. We may write that ΔΔG[‡] = ΔG[‡]_{Br} - ΔG[‡]_{Cl}. The ΔG[‡]_{Br} and the ΔG[‡]_{Cl} are the free activation energy of the elimination of bromo and chloro radicals from the radical **6**, respectively. It seems reasonable to assume the ΔS[‡] of the elimination reaction of bromo radical is similar to that of the elimination reaction of chloro radical. Therefore, the ΔΔG[‡] could be expressed in terms of the ΔΔH[‡]. It is also plausible to assume the value of ΔΔH[‡] of the free radical reaction is close to the difference of the bond dissociation energy between C-Cl bond and C-Br bond. The bond dissociation energy of C-Cl bond is 71 kcal/mol and that of C-Br bond is 57 kcal/mol.¹¹ Then, the value of ΔΔH[‡] is about 14 kcal/mol. Theoretically, the k_{Br}/k_{Cl} ratio would be 10¹⁰, in the extreme. However, the k_{Br}/k_{Cl} ratio is only 14.3 experimentally. This experimental value is too small to compare with the theoretical value. Therefore, the mechanism of S_H2' reaction seems not consistent with the stepwise mechanism as Russell proposed. This suggests that the S_H2' reaction might not proceed via the stepwise mechanism. The k_{Br}/k_{Cl} ratios are greater than unity for both intramolecular and intermolecular leaving group effects, and the S_H2' reactions seem to favor the concerted mechanism.

The value of intermolecular leaving group effect is smaller than that of intramolecular leaving group effect in free radical S_H2' reaction, although they were measured in different solvents. The difference is due mainly to solvation of the transition state. Both chloro and bromo leaving groups suffer the same extent of solvation in the transition state of compound **3**, because they are on the same molecule. The intramolecular leaving group effects should not be affected by the solvent effect. Thus, the k_{Br}/k_{Cl} ratio of compound **3** measured in DMSO would be close to that measured in CH_3CN . The transition state with a smaller and poor chloro leaving group has a larger charge density than that with a bromo leaving group. Therefore, the transition state of compound **1** is relatively better solvated than that of compound **2**. The decreasing k_{Br}/k_{Cl} ratios in the intermolecular leaving group effect can be attributed to the acceleration of compound **1** due to the better solvation in the transition state.

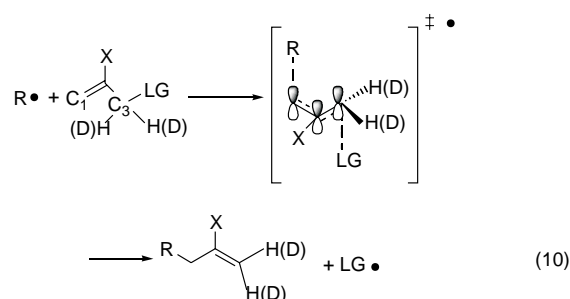
Secondary α -deuterium kinetic isotope effects in free radical S_H2' reactions

Secondary α -deuterium kinetic isotope effects have been widely used to determine how changing a substituent on the nucleophile, the substrate, or the leaving group alters the structure of the transition state of substitution reactions (eq 9).¹²



The magnitude of a secondary α -deuterium kinetic isotope effect is determined by the changes that occur in both the $C_\alpha\text{-H(D)}$ stretching and out-of-plane bending vibrations when the reactant is converted into the transition state.¹³ Westaway and Ali pointed out^{12a} that the energy of these bending vibrations is directly related to the amount of steric crowding around the $C_\alpha\text{-H}$ bonds. The amount of steric crowding around the $C_\alpha\text{-H}$ bonds in the trigonal bipyramidal transition state can only be altered significantly by changing the length of one or both of the nucleophile--- α -carbon or α -carbon---leaving group bonds. Thus, the magnitude of the secondary α -deuterium kinetic isotope effect should be a measure of the nucleophile---leaving group distance in an

S_N2 transition state. S_N2 reaction can exhibit $k_H/k_D > 1$ when the separation between the two proximal atoms of nucleophile and leaving group is relatively long, thus forming a comparatively loose transition state.^{12a-b,14} If the free radical S_H2' reaction proceeds the concerted process as the S_N2 reaction does, it is likely that the free radical S_H2' reaction should progress as shown in eq 10, and the value of secondary α -deuterium kinetic isotope effect would be expected to be greater than unity. There is obvious difference between the S_H2' reaction and the S_N2 reaction. The difference lies in that the reaction center includes three carbons in eq 10 instead of one carbon in eq 9. Therefore, C_3 is α carbon for the leaving group and C_1 is α carbon for the alkyl radical, respectively, in the S_H2' reaction.



We try to use secondary α -deuterium kinetic isotope effect to investigate whether or not the rupture of the leaving group occurs in the transition state of free radical S_H2' reactions. The two deuteriums are placed at α carbon of the leaving group (C_3) to measure secondary α -deuterium kinetic isotope effects. The secondary α -deuterium kinetic isotope effects of the following two pairs of substrates, compound **1a** and 3,3-d₂-3-chloro-1-propene (**7**), compound **1b** and 3,3-d₂-3-chloro-2-methyl-1-propene (**8**), are also determined indirectly by the competitive technique as described before. A summary of the relative rate data is presented in Table 1. The relative rates of k_{1b}/k_7 and k_{1a}/k_8 are 0.92 and 1.60, respectively. The secondary α -deuterium kinetic isotope effects are obtained by simple calculation, and the results are shown in Table 3. When the substituents are H and CH_3 , the values of k_H/k_D are 1.22 (k_{1a}/k_7) and 1.20 (k_{1b}/k_8), respectively.

Kim et al. reported that cyanide abstractions from benzyl isocyanides by radicals took place in a concerted mechanism and secondary α -deuterium kinetic isotope effects, k_H/k_D , were between 1.075 and 1.259.¹⁵ Therefore, we might suggest that the free radical S_H2' reactions might proceed the concerted mechanism based on the data of the leaving group effects and the kinetic isotope effect.

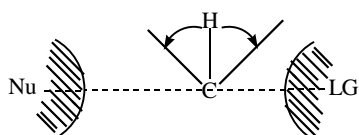
Table 3. The secondary α -deuterium kinetic isotope effects of $H_2C=CHX-CH_2(D_2)Cl$ in the S_H2' reactions

Substituent X	k_H/k_D
H	1.22 ^a
CH ₃	1.20 ^b

^a $k_H/k_D(k_{1a}/k_7) = k_{1b}/k_7 \div k_{1b}/k_{1a}$ ^b $k_H/k_D(k_{1b}/k_8) = k_{1a}/k_8 \times k_{1b}/k_{1a}$ k_{1b}/k_7 , k_{1b}/k_{1a} and k_{1a}/k_8 were cited from Table 1.

The magnitude of the secondary α -deuterium kinetic isotope effect is a measure of the nucleophile-leaving group distance in the S_N2 reaction transition state. Is this the same as in the free radical S_H2' reaction? The answer is obviously not. If we look at eq 9 and eq 10 precisely, the CD_2 group is at α position in both the nucleophile and leaving group in eq 9. However, the CD_2 group is at α position of the leaving group only in eq 10. The magnitude of the secondary α -deuterium kinetic isotope effect (the change in the $C_\alpha-H(D)$ out of plane of vibrations when the reactants are converted into the transition state) might depend on the looseness of the transition state. The looseness of the transition state of the S_N2 reaction is dependent upon the distance between the nucleophile and the leaving group. On one hand, the change in the $C_\alpha-H(D)$ out of plane of vibrations is not dependent entirely upon the looseness of the transition state in the free radical S_H2' reaction. Actually, the change in the $C_\alpha-H(D)$ out of plane of vibrations is influenced only by the partial structure of the transition state of the S_H2' reaction. The C_1 , C_2 and C_3 carbons would be in the same plane when the reactants are converted into the transition state (eq 10), and two $C_\alpha-H(D)$ bonds are also in the same plane. On the other hand, the leaving group would be perpendicular to this plane. Westaway et al. indicated that the magnitude of the secondary α -deuterium kinetic isotope effect was determined by the length of only the shorter reacting bond if the S_N2 transition state were unsymmetrical.¹⁶ In other words, the change in the $C_\alpha-H(D)$ out of plane of vibrations might only depend on the length of the shorter reacting bond rather than on the nucleophile-leaving group distance (Fig. 1).

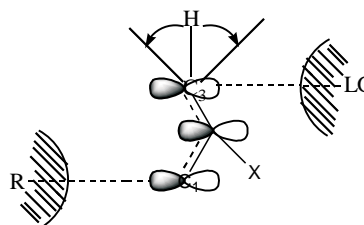
Calculation for the addition of a methyl radical to

Fig. 1. $C_\alpha-H(D)$ out of plane bending for an unsymmetrical S_N2 transition state.

ethene suggests that the incoming radical approaches along a trajectory perpendicular to the nodal plane of the π system at approximately the tetrahedral angle.¹⁷ It allows us to assume the *t*-butyl radical addition to double bond is similar to what the methyl radical does; therefore, it is plausible to assume that a carbon centered radical undergoes an S_H2' reaction via a transition state which might be close to Fig. 2.

Comparing Fig. 2 with Fig. 1, the $C_\alpha-H(D)$ out of plane of vibrations in an S_H2' reaction transition state is similar to that in the unsymmetrical S_N2 transition state. It is obvious that the $C_\alpha-H(D)$ out of plane of vibrations around C_3 carbon--leaving group is more crowding than the other side around C_3 carbon from Fig. 2. Thus, the secondary α -deuterium kinetic isotope effect in an S_H2' reaction is dependent on the length of the shorter reacting bond, which in this case is the C_3 carbon--leaving group distance. The magnitude of the secondary α -deuterium kinetic isotope effect in an S_H2' reaction might indicate the looseness between the reaction center (C_3) and the leaving group in the transition state.

The secondary α -deuterium kinetic isotope effects in Table 3 show $k_H/k_D > 1$ regardless of the substituents. Seltzer¹⁸ reported that the secondary α -deuterium isotope effect in the free radical cleavage of azo-bis- α -phenylethane was found to be 1.27. He also reviewed a large body of data on secondary α -deuterium isotope effects. The isotope effects of the reactions, involving a rate controlling unimolecular bond scission, are remarkably constant. The constancy of this isotope effect, observed in these cases, stems from the similarity in the changes of the $C_\alpha-H$ vibrational frequencies in going from their respective ground states to transition states. Moreover, the $C_\alpha-H$ frequencies are relatively insensitive to the chemical nature of substitution at that carbon atom. Therefore, it seems likely that the secondary α -deuterium kinetic isotope effects are unaffected by the substituent at the β -carbon atom in an S_H2' reaction. The reason is that the substituent at the β -carbon atom would not affect the crowding between the reaction center (C_3) and the leaving group in the transition state.

Fig. 2. $C_\alpha-H(D)$ out of plane bending for an S_H2' reaction transition state.

CONCLUSION

The values of the intramolecular and intermolecular leaving groups effects are both greater than unity in the free radical S_H2' reactions, and the values of secondary α -deuterium kinetic isotope effects are 1.20 to 1.22. All data favor the S_H2' reactions to proceed with the concerted mechanism rather than the stepwise mechanism. The magnitude of the secondary α -deuterium kinetic isotope effect, in general, is a measure of the nucleophile-leaving group distance in the S_N2 reaction transition state. However, Westaway et al. pointed out that the magnitude of the secondary α -deuterium kinetic isotope effect was dependent upon the length of only the shorter reacting bond if the S_N2 transition state were unsymmetrical. Therefore, the magnitude of the secondary α -deuterium kinetic isotope effect in an S_H2' reaction might indicate the looseness between the reaction center and the leaving group in the transition state rather than the distance between the alkyl radical and the leaving group.

EXPERIMENTAL SECTION

Analytical gas chromatography was performed using a Perkin-Elmer Autosystem with a DB-5 column (0.25 μ M, 60 M) and a flame ionization detector. 1H NMR spectra were recorded on a 300 MHz VXR FT-NMR spectrometer with tetramethylsilane as the internal standard. GCMS were recorded on a Quattro GCMS 5022 spectrometer or HP 5890 Series II Gas Chromatograph with HP 5972A MSD. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected.

Materials

Solvents were purchased from Riedel-de Haen and Mallinckrodt. Dimethyl sulfoxide (DMSO) was distilled from calcium hydride and stored over 4A molecular sieves under nitrogen; diethyl ether, and tetrahydrofuran were distilled from sodium metal. Other solvents were purchased and used without purification. Allyl chloride, 2-methylallyl chloride, allyl bromide, 2-methylallyl bromide, *t*-butyl chloride, and biphenyl were purchased from Aldrich Chemical Company. In most cases, the reagents were used without further purification. Organomercurials were synthesized by the standard Grignard procedure.¹⁹ 3,3- d_2 -3-chloro-1-propene (**7**)²⁰ and 3,3- d_2 -3-chloro-2-methyl-1-propene (**8**)²¹ were synthesized by the methods reported in the literature. The 96% pure deuterium of compound **7** was obtained. GCMS: m/z (relative

intensity): 80 ($M+2^+$, 14), 78 (M^+ , 41), 43 (100). 1H NMR ($CDCl_3$): 5.99-5.94 (m, 1H), 5.40-5.20 (m, 2H), 4.05 (CH_2Cl) < 4%. The deuterium purity of compound **8** was greater than 96%. GCMS: m/z (relative intensity): 94 ($M+2^+$, 8), 92 (M^+ , 24), 57 (100). 1H NMR ($CDCl_3$): 5.05 (s, 1H), 4.92 (s, 1H), 3.90 (CH_2Cl) < 4%, 1.83 (s, 3H).

General Procedure for Competitive Photostimulated Reactions of 2-Substitutedallyl Halides with *t*-Butylmercury Chloride⁸

A pair of 2-substitutedallyl halides (1.0 mmol), *t*-BuHgCl (0.1 mmol) and internal standard (0.05 mmol of biphenyl) were dissolved in 1 mL of nitrogen-purged dry dimethylsulfoxide. The solution was divided into dry and nitrogen-purged four quartz tubes (0.25 mL in each tube) each equipped with a rubber septum. The tubes were irradiated at 35-40 °C with a 100 W UV lamp placed about 20 cm from the reaction tubes. Reaction tubes were removed at various times and the yields of the substitution products were determined by Gas Chromatography. Identification of substitution products was confirmed by comparison of their GCMS data with those of the authentic compounds synthesized by the method described in our previous reports.^{8,11} GLC yields were determined by using an internal standard (biphenyl) and were corrected with predetermined response factors. The relative rate ratios of the competitive reactions are shown in Table 1.

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