The Competitive Reactions between Electron Transfer and Radical Addition in Free Radical Reactions

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The photolytic re ac tions of 2-substituted allyl chlo ride with *t*-BuHgCl in different sol vents were in vestigated. The reactions proceed the S_H2' reaction mech a nism except the substituent is a strong electron-releasing group. The electron transfer process becomes more competitive with the radical addition process when the substituent is a strong electron-releasing group. When the substituent is a strong electron-releasing group such as -CH₂SiMe₃, the reaction in CH₃CN shows pronounced electron transfer process while the reaction in DMSO or THF in volves both of the S_H2' and the electron transfer processes. The reaction is sol vent dependent. An electron transfer mech anism is discussed.

INTRODUCTION

In the last two de cades, the ad di tion re ac tions of carbon-centered rad i cals to alkenes have been in ten sively in vesti gated from both the the oret i cal and practical points of view.¹ The S_H2' re ac tion mech a nism of *t*-BuHgCl with allyl de riv atives was pro posed by Rus sell et al.² as shown in Scheme I.

Scheme I

$H_2C=CXCH_2CI + R \cdot \longrightarrow RCH_2CXCH_2CI$	(1)

 $RCH_2CXCH_2CI \longrightarrow RCH_2CX=CH_2 + CI \cdot$ (2)

$$RHgCI + CI - \longrightarrow HgCl_2 + R - (3)$$

The alkyl rad i cal adds to the ter mi nal car bon of the dou ble bond to form an in ter me di ate rad i cal, which un der goes fast β -elim i na tion of the leav ing group Cl· in a chain pro cess. In ourprevious investigation,³ the re ac tions of *t*-BuHgCl with 2-substituted allyl chlo ride **1**, un der photolytic con di tions, gave the prod ucts **2** in good yields. The re ac tion de picted in equa tion (4) is be lieved to pro ceed by the S_H2' re action mechanism.

$$X \rightarrow CI + t-BuHgCI \rightarrow DU \rightarrow X \rightarrow Bu-t \qquad (4)$$

$$1 \qquad 2$$

$$1a \quad 1b \quad 1c \quad 1d \quad 1e \rightarrow X \rightarrow Bu-t \qquad (4)$$

$$X = H \quad Me \quad CI \quad CH_2CI \quad CH_2SIMe_3$$

Cor re la tion of log k/k_0 for 2-substituted allyl chlo ride with \mathbb{Q}_m gave the p value of 3.39. This ob ser va tion is con sistent with the nucleophilic char ac ter of the *t*-butyl radical. The rate of the *t*-butyl rad i cal ad di tion to 2-substituted allyl chlorides **1** pro ceeds by the S_H2' mech a nism and is gov erned by the po lar effect of sub stitu ents. The elec tron-withdrawing sub stitu ents in crease and the elec tron-releasing sub stitu ents de crease the re ac tion rate of the free rad i cal S_H2' reaction. There fore, the re ac tion rates of the S_H2' reactions should be slug gish when the substituent is the elec tron-releasing group such as $-CH_2SiMe_3$ (the \mathbb{Q}_m is -0.16). In the pres ent re port, we in vest ig gate the photolytic re ac tions of 2-trimethylsilylmethyl allyl chlo ride (**1e**) with *t*-BuHgCl in differ ent sol vents. The re ac tion rates are re ally slug gish when the re ac tions are carried out in DMSO or THF. How ever, an anom aly is found when the re ac tions are per formed in acetonitrile so lution.

RESULTS AND DISCUSSION

We found that the re ac tions of *t*-BuHgCl with the compound **1**, un der photolytic con di tions, gave the prod ucts **2** in good yields ex cept the X was $-CH_2SiMe_3$ (Ta ble 1). The yields of sub sti tu tion prod uct **2e** were all low in differ ent solvents. The photolytic ex per i ments were car ried out with the com pound **1e** (at least 10 times with re spect to *t*-BuHgCl in CH_3CN or Me_2SO or THF) and after the period of time in dicated in the Ta bles determining the rel a tive amounts of products (which are shown in equation 5) by GC.



Substrate CH ₂ =C(X)CH ₂ Cl	Conditions ^a	CH ₂ =C(X)CH ₂ Bu-t % Yields ^b		
		DMSO	CH ₃ CN	THF
X=H	2 h	45	42	59
X=CH ₃	2 h	28	20	55
X=Cl	2 h	90	46(3h)	54
X=CH ₂ Cl	2 h	93	59	37
$X = CH_2SiMe_3$	2 h	2	5	10

Table 1. Reactions of Compound 1 with t-BuHgCl at 35-45 °C in Different Solvents

^a Substrate (1 M) and mercurial (0.1 M) in nitrogen-purged dry solvents were irradiated with a 100 W UV lamp ca. 20 cm from the reaction quartz tube. Each reaction was run at least three times. Error $\pm 4\%$.

^b The yield was determined by GC and based on the amount of mercurial.

Iden ti fi cation of substitution products was confirmed by com par i son of their GCMS data with those of the au thentic com pounds syn the sized by known liter a ture meth ods.³ The re sults are shown in Ta ble 2. It seems un likely that the photostimulated re ac tion of com pound **1e** with *t*-BuHgCl pro ceeds the S_H2' process as a major path way.

The photolytic re ac tion of the com pound **1e** with *t*-BuHgCl in Me₂SO so lu tion gave the low yields of sub sti tution prod ucts, which in cluded a small amount of 2-tri methylsilylmethyl-4,4-dimethyl-1-pentene (**2e**), hexamethyl disilox ane (**3**), and 2,4,4-trimethyl-1-pentene (**2b**). There were sim i lar re sults in THF so lu tion. How ever, there were much different re sults ob served when the re ac tions were car ried out in CH₃CN so lu tion. The com pounds **3** and **1b** (2-methylallyl chloride) were the ma jor prod ucts, and a small amount of com pound **2b** and none of com pound **2e** were de tected. A trace of 2-methylpropene was de tected in all the photolytic re ac tions. Be fore the photolysis, the sol vent and quartz tube were deoxygenated by a method re ported in the lit er a ture.² It was sur pris ing that the com pound **3** was a ma jor prod uct in the photolytic re ac tions. The re ac tion mix ture was deoxygenated very care fully and photolyzed un der ni tro gen; the ma jor prod ucts were the same as be fore, but the com pound **3** was not de tected. In stead, a trace of hexamethyldisilane and trimethylsilane were ob served.

The S_H2' sub sti tuted product 2e was not detected in the photolytic re actions of the com pound 1e with *t*-BuHgCl in CH₃CN. Thus, it is hard to ratio nal ize this re action by the S_H2' process. The possible mech anism of the photolytic re actions of the com pound 1e with *t*-BuHgCl in CH₃CN is proposed as in Scheme II. The *t*-butyl radical, which is generated from the photolysis of *t*-BuHgCl, might add to the double bond (equation 7) or might do an electron trans fer with the com pound 1e to give the radical an ion 4 and *t*-butyl cation (equation 8). These two processes are competiative with each other. How ever, the *t*-butyl radical does not add to the double bond in stead of proceed ing the single electron trans fer with the com pound 1e. The radical anion 4 undergoeselimination

Table 2. Reactions of Compound 1e with t-BuHgCl at 35-45 °C in Different Solvents

Conditions ^a	% product $2e^b$	% product 3 ^b	% product 1b ^b	% product 2b ^b
2 h Me ₂ SO	2	1	0	1
4 h Me ₂ SO	4	5	0	6
6 h Me ₂ SO	2	6	0	7
8 h Me ₂ SO	0.4	7	0	8
2 h CH ₃ CN	0	197	432	4
4 h CH ₃ CN	0	277	608	11
6 h CH₃CN	0	291	639	15
8 h CH ₃ CN	0	315	696	18
1 h THF	4	12	0	12
2 h THF	10	15	0	14
3 h THF	6	24	0	22

^a Substrate (1 M) and mercurial (0.1 M) in nitrogen-purged dry solvents were irradiated with a 100 W UV lamp ca. 20 cm from the reaction quartz tube. Each reaction was run at least three times. Error ±4%.

^b The yield was determined by GC and based on the amount of mercurial.

Scheme II

$$2 tBuHgCl \longrightarrow 2 tBue + HgCl_2 + Hg^0$$
(6)

7)

$$\overbrace{CH_2}^{CH_2} \xrightarrow{\text{proton}} \overbrace{-CI}^{CH_3}$$
(10)

$$\xrightarrow{\mathsf{CH}_3} \xrightarrow{t \cdot \mathsf{Bu} \bullet} \xrightarrow{\mathsf{CH}_3} \xrightarrow{\mathsf{H}_3} + \mathsf{CI} \bullet \tag{11}$$

$$\begin{array}{c} -SiMe_3 & Me_3Si \bullet \\ -CI & SET & -CI \\ 1e & \end{array} \right] + Me_3Si$$
 (12)

$$\begin{array}{c} \overbrace{\qquad}^{\text{SiMe}_3 \text{ Me}_3\text{Si} \bullet} \\ \xrightarrow{\qquad} Bu-t \quad \text{SET} \\ 2e \end{array} \begin{bmatrix} \overbrace{\qquad}^{\text{SiMe}_3} \\ & t-Bu \\ & T \end{bmatrix} + Me_3\text{Si} \\ (13)$$

$$\xrightarrow{CH_2}_{t-Bu} \xrightarrow{\text{proton}} \xrightarrow{CH_3}_{Bu-t} (15)$$

of Me₃Si· to form the an ion5 which ab stracts a pro ton to give the product 1b. The addition reaction of t-butyl radical with the product 1b forms the product 2b. The Me₃Si · might act as a chain car rier which re acts with the com poundle via a sin gle elec tron trans fer process to give radical an ion4, which contin ues the chain (equa tion 12), and the trimethylsilyl cat ion which might be re spon si ble for the for ma tion of hexamethyldisiloxane. The Me₃Si · could also cou ple it self to form hexamethyl disilane or ab stract a hy dro gen to pro duce trimethylsilane. The trimethylsilyl cat ion might lose a pro ton to form a vol a tile com pound, which was not de tected by GC. There are two pos si ble ways to give the prod uct 2b, one is t-butyl rad ical ad di tion to the com pound **1b**, the other is the com pound 2e via the elec tron trans fer pro cess to pro duce the prod ucts 2b. The rad i cal an ion7 and trimethylsilyl cat ion are produce by the elec tron trans fer re ac tion be tween the com pound 2e and trimethylsilyl rad i cal. The rad i cal an ion 7 undergoes elimination of trimethylsilyl rad i cal to form the an ion **8**, which ab stracts a pro ton to pro duce the prod uct **2b**. Which one is the ma jor pro cess to pro duce prod uct **2b**? This part will be dis cussed later.

Giese⁴ has reported that mainly the polar effects of the sub stitu ents con trol the rates of ad di tion of alkyl rad i cals to alkenes. The substituent ef fects can be de scribed by FMO.⁵ There fore, the en ergy gap be tween the SOMO of a free rad ical and the LUMO of the alkene is a de ci sive fac tor to de termine the reaction rate. Elec tron-releasing sub stitu ents in the alkene, which raise the LUMO en ergy, de crease the ad di tion rate by in creasing the SOMO-LUMO en ergy gap. In our previous investigation,³ the p value was 3.39 for the S_H2' reactions of 2-substituted allyl chlo rides with t-BuHgCl. The substituent ef fect is sub stan tial in the free rad i cal S_H2' re action. The rad i cal ad di tion pro cess be comes more diffi cult when the substituent is a good elec tron-releasing group such as $-CH_2SiMe_3$ whose O_m value is -0.16. The electron trans fer path way (equation 7) be comes more com pet i tive with the rad i cal ad di tion pro cess (equa tion 8) when the substituent is -CH₂SiMe₃, al though the elec tron trans fer process is en ergy unfavorable.6

There are three pos si ble ways to pro duce the prod uct **1b**. One is the com pound **1e** which is photolyzed to give the trimethylsilyl radi cal and $H_2C=C(CH_2Cl)CH_2$ which abstracts a hydrogen to form the product 1b. The other two possi ble ways are that com pound le re acts with ei ther t-BuHgCl or t-Bu· via the elec tron trans fer process. The first pos si ble way might be ex cluded be cause the start ing ma te rial 1e was de tected only in the solution after the photolytic reaction of the com pound 1e alone. The elec tron trans fer re ac tion of the com poundle with t-BuHgCl might be eliminated be cause the starting materialle was left in the solution and no other products were found after the reaction of the compound 1e with t-BuHgCl was heated to 45 °C in the ab sence of light. The reac tion of the com pound le with t-BuHgCl in the pres ence of radical scaven ger TEMPO (2,2,6,6-tetramethyl-1-piperidinyl oxy, free rad i cal) was car ried out un der photolytic con ditions. The re ac tion was in hib ited by TEMPO and only the com pound **1e** was left in so lu tion af ter photolysis. This also in di cates that an elec tron trans fer re ac tion be tween the compound 1e and t-BuHgCl does not take place and sug gests that an elec tron trans fer process might have oc curred be tween the com pound 1e and t-butyl radical. The ion ization potential is 6.70-6.92 eV for the *t*-butylradical.⁷ Un for tunately, the ionization potential of the compound 1e was not found in the literature. However, the ionization potentials are 8.85^8 (or 9.0)⁹ eV for 3-trimethylsilyl-1-propene and 10.34¹⁰ (or 11.23)¹¹ eV for allyl chlo ride. It seems plau si ble if we as sume the ion ization potential of the compound 1e is be tween 8.85 eV and 11.23 eV. The ion iza tion po ten tial of the t-butyl rad i cal is less than that of the com pound 1e; there fore the t-butyl rad ical loses an elec tron more easily than the com pound le does. It is likely that the elec tron trans fer pro cess could oc cur between the com pound 1e and t-butyl rad i cal (equation 8) on the basis of the ion ization potential although the electron affin ity of the com pound **1e** is un known. The trimethylsilyl rad i cal is a chain car rier, which re acts with the com pound 1e via the electron transfer process to give radical an ion 4, which con tin ues the chain, and trimethylsilyl cat ion which might form hex amethyldisiloxane. It seems rea son able to ratio nal ize the elec tron trans fer process of the compound 1e with the tri methylsilyl rad i cal, whose ion iza tion po ten tial is 6.42 eV, ¹² in terms of ion iza tion po ten tial. There is an other in direct evidence to clarify that the trimethylsilyl radical is a chain car rier in this re action. The yields of products 3 and 1b are greater than 100% based on the amount of t-BuHgCl (Table 2). There is nothing that oc curs in the course of the photolytic reaction of the compound 1e alone; this shows that the tri meth ylsilyl rad i cal is not gen er ated di rectly from the photo lysis of the com pound le and should be pro duced by an elec tron trans fer process. We might suggest that the reaction should prog ress a chain pro cess and that the trimethylsilyl rad i cal is a chain car rier. The re ac tion mix ture was photolyzed un der ni tro gen, and the com pound 3 was not de tected; in stead, a trace of hexamethyldisilane and trimethylsilane were ob served. The yield of hexamethyldisilane should almost ap proach to a half of that of the prod uct 1b if the trimeth ylsilyl rad i cal is not a chain car rier. How ever, only a trace of hexamethyldisilane was detected, ow ing to that most of the trimethylsilyl rad i cal pro ceeded an elec tron trans fer pro cess to form the trimethylsilyl cat ion which might not produce hexamethyldisilane. All the data fa vor that the tri methylsilyl rad i cal is a chain car rier.

We are sur prised that the hexamethyldisiloxane is a major prod uct in this re action be cause the re action is car ried out in the con di tion of wa ter and air free (see ex per i men tal section). How ever, when the re action is proceeded un der ni trogen, the hexamethyldisiloxane is not de tected. Sim i lar re sults were found in the works of Fearon¹³ and Sakurai.¹⁴ Fearon and Young reported¹³ that the reaction of triphenylsilyl halides with so dium naphthalenide yielded mainly hexaphenyl disiloxane and a small amount of 1,4-bis(triphenylsilyl)- 1,4-dihydronaphthalene. The mechanism in volving an ini tial elec tron trans fer to pro duce a triphenylsilyl rad i cal was proposed. Sakurai¹⁴ in di cated that the re action of phenyl di meth-

yl chlorosilane and so dium naphthalenide pro duced 1,2-diphen yltetramethyldisilane and bis(phenyldimethylsilyl)oxide as the main prod ucts. Fearon and Young¹³ sug gested that hexaphenyldisiloxane had arisen from side re ac tions of triphenylchlorosilane with ad ven titious water ad sorbed into the ap pa ra tus, al though great pains were taken with the dry ing and purification of materials used. However, Sakurai¹⁴ suggested that disiloxane might come from the silyl rad i cal it self with an oxygen donor such as solvent molecules. If the hexamethyldisiloxane, which ap peared as Sakurai sug gested when the silyl rad i cal it self re acted with an ox y gen do nor, was produced in the reaction of compound le with t-BuHgCl un der photolytic con di tions, then the chain re ac tion was inter rupted (equation 12). The yields of com pound3 should not be as high as 50% and the yields of the prod uct1b should not be greater than 100% (based on the amount of *t*-BuHgCl); never the less, the yields of com pound3 and 1b are all greater than 100% in CH₃CN (Ta ble 2). It is un likely that hexamethyl disiloxane is pro duced from the re ac tion of the trimethylsilyl radical with an ox y gen do nor in the solution. There fore, the com pound 3 might come from the trimethylsilyl cat ion with an ox y gen do nor in the so lu tion, al though much ef fort was spent for the dry ing and purification of materials used. When the reaction was carried out undernitrogen, most of the trimethylsilyl rad i cal un der went the elec tron trans fer re action to give trimethylsilyl cat ion, which could not give the com pound3 be cause an ox y gen do nor com pletely free in this condition might lose a proton to produce vol a tile compounds which were not de tected by GC or GCMS. There fore, only a small amount of trimethylsilyl rad i cal, which was left in the so lution, might cou ple with it self to pro duce hexameth yldisilane or ab stract a hy dro gen to form trimethylsilane; this might ra tio nal ize that only a trace of hexamethyldisilane and trimethylsilane were de tected when the re ac tion was performed un der ni tro gen. The trimethylsilyl cat ion might re act with wa ter to give trimethylsilanol,¹⁵ which might de hy drate to form hexamethyldisiloxane.¹⁶ As the yields of hexamethyl disiloxane are a lit tle less than one half of those of the compound 1b (Ta ble 2), this also might sug gest that the hexameth yldisiloxane is produced from the trimethylsilyl cation.

The photolytic re ac tions of com pound **1e** with *t*-BuHgCl in Me₂SO or THF give low yields of the S_H2' substituted prod uct **2e** and the elec tron trans fer prod ucts **3** and **2b**. This sug gests that the free rad i cal ad di tion and the elec tron transfer re ac tion oc cur si multa neously in Me₂SO or THF. These two pro cesses seem to com pete with each other, but both reac tions are slug gish in Me₂SO or THF (Ta ble 2). The compound **2b** might be formed ei ther from the com pound **1b** by radical addition or from the product 2e by an elec tron trans fer process. If the product2b all comes from the product1b, that means the en tire com pound 1b con verts to the prod uct 2b, since the yields of the prod uct1b are zero in the course of the reaction. The reaction proceeds the electron transfer process, and then the yield of the prod uct 3 should be near one half of that of the prod uct 2b. How ever, the yields of the prod uct 3 are al most equal to those of the prod uct 2b at different reaction times in DMSO or THF (Ta ble 2). The yields of the product 3 are greater than the expected values. This in dicates that the product $\mathbf{3}$ is not only contributed from equation (12). The yield of the prod uct3 would not be af fected if the prod uct2b comes from the product **1b**, but the yield of the product **3** would in crease if the prod uct 2b is converted from the product 2e via the elec tron trans fer process. This might im ply that there is an other elec tron trans fer process in the mech a nism be sides that in equa tion (12). The prod uct 1b was not observed in the course of the re action, and the yields of the product 2e de creased while the yields of the prod uct 2b increased. This might in di cate that the com pound 2b might be de rived from the prod uct 2e by the electron trans fer process. We might con clude that the prod uct 2b would be con trib uted from two sources, one is from the prod uct 2e via the elec tron trans fer pro cess and the other is from the prod uct 1b by free radi cal ad di tion. It is still un clear what causes the difference between the photolytic reaction of the compound 1e in CH₃CN and in DMSO.

EXPERIMENTAL SECTION

An alytical gas chromatog raphy was performed using a Perkin-Elmer Autosystem with a DB-5 col umn (0.25 μ M, 60 M) and a flame ion ization detector. ¹H NMR spectra were recorded on a 300 MHz VXR FT-NMR spectrom eter with tetramethylsilane as the inter nal stan dard. GCMS were recorded on a Quattro GCMS 5022 spectrom eter or HP 5890 Se ries II Gas Chromatograph with HP 5972A MSD. Melting points were determined on a Thomas-Hoover capillary melting point ap para tus and were un cor rected. GLC yields were deter mined by using an inter nal stan dard (biphenyl) and were corrected with predetermined response factors.

Materials

Solvents were purchased from Riedel-de Haen and Mallinckrodt. Dimethyl sulfoxide (DMSO) and acetonitrile were dis tilled from cal cium hy dride and stored over 4A molec u lar sieves un der ni tro gen; di ethyl ether, and tetra hydrofuran were dis tilled from so dium metal. Other sol vents were purchased and used withoutpurification. Allyl chloride, 2-methylallyl chloride, 2-chloroallyl chloride, 2-chloro methyl allyl chloride, 2-(trimethylsilylmethyl)allyl chloride, and t-butyl chloride, TEMPO(2,2,6,6-tetramethyl-1- piperidinyloxy, free rad i cal), hexamethyldisilane, and hexamethyl disiloxane, biphenyl were purchased from Aldrich Chemical Com pany. In most cases, the re agents were used with out further puri fi cation. Organomercurials were syn the sized by the standard Grig nardproce dure.¹⁷

General Procedure for Photostimulated Reactions of 2-SubstitutedAllyl Chloride with *t*-Butylmercury Chloride in Different Solvents (Tables 1 and 2)

2-substitutedallyl chlo ride (1.0 mmol), t-BuHgCl (0.1 mmol) and in ter nal stan dard (0.05 mmol of biphenyl) were dis solved in 1 mL of ni tro gen-purged dry sol vents. The so lution was di vided into four dry and ni tro gen-purged quartz tubes (0.25 mL in each tube) with each equipped with a rubber sep tum. The tubes were ir ra di ated at 35-40 °C with a 100 W UV lamp placed about 20 cm from the re ac tion tubes. Reac tion tubes were re moved at var i ous times and the yields of the sub stitution products were determined by gas chromatography. Identification of substitution products was confirmed by com par i son of their GCMS data with those of the au thentic compounds syn the sized by the methods reported in the literature.¹⁸ The follow ing products were obtained from the reactions out lined in Table 1.4,4-Dimethyl-1-pentene² (2a): bp 71-72 °C/760 mmHg; ¹H NMR (300 MHz, CDC1₃) δ 6.0-5.6 (m, 1 H), 5.1-4.9 (m, 2 H), 1.92 (d, J = 7.5 Hz, 2 H), 0.87 (s, 9 H); GCMS m/z (rel a tive in ten sity) 98 (M⁺, 1), 83 (2), 57 (100), 55 (30), 41 (48), 39 (15). 2,4,4-trimethyl-1-pentene (**2b**): bp 101-103 °C/760 mmHg; ¹H NMR (300 MHz, CDC1₃) δ 4.83 (s, 1H), 4.63 (s, 1H), 1.94 (s, 2H), 1.77 (s, 3H), 0.93 (s, 9H); GCMS (EI) *m/z* (relative intensity) 112 (M⁺, 16.18), 97 (18), 57 (100), 55 (56). 2-chloro-4,4-dimethyl-1-pentene (2c): ¹H NMR (300 MHz, CDC1₃) δ 5.26 (s, 1H), 5.06 (s, 1H), 2.26 (s, 2H), 1.0 (s, 9H); GCMS (EI) *m*/*z*(relative intensity) 134 ((M+2)⁺, 1.01), 132 (M⁺, 3.14), 117 (5), 57 (100), 53 (11), 41 (71). 2-chloromethyl-4,4-dimethyl-1-pentene (2d): ¹H NMR (300 MHz, CDC1₃) § 5.28 (s, 1H), 4.96 (s, 1H), 4.06 (s, 2H), 2.10 (s, 2H), 0.94 (s, 9H); GCMS (EI) m/z (relative in ten sity) 148 ((M+2)⁺, 0.29), 146 (M⁺, 0.79), 133 (1.79), 131 (7), 110 (10), 95 (50), 67 (30), 57 (100), 53 (45), 41 (79). 2-trimethylsilylmethyl-4,4-dimethyl-1-pentene (2e): ¹H NMR (300 MHz, CDC1₃) §4.51 (s, 1H), 4.13 (s, 1H), 1.86 (s, 2H), 1.57 (s, 2H), 0.93 (s, 9H), 0.02 (s, 9H); GCMS (EI) m/z $(relative intensity) 169((M-15)^+, 3.9), 128(14), 73(100), 57$

(19), 45 (8.9).

The Photolytic Reactions of 2-Trimethylsilylmethyl Allyl Chloride in Different Solvents

2-Trimethylsilylmethyl allyl chlo ride (1.0 mmol), and in ter nal stan dard (0.05 mmol of biphenyl) were dis solved in 1 mL of ni tro gen-purged dry sol vents. The so lu tion was divided into four dry and ni tro gen-purged quartz tubes (0.25 mL in each tube) with each equipped with a rub ber sep tum. The tubes were ir ra di ated at 35-40°C with a 100 W UV lamp placed about 20 cm from the re ac tion tubes. Re ac tion tubes were re moved at var i ous times and only the start ing ma te rial was de tected by GC or GCMS.

The Photolytic Reactions of 2-Trimethylsilylmethyl Allyl Chloride with *t*-Butylmercury Chloride and TEMPO in Different Solvents

2-Trimethylsilylmethyl allyl chlo ride (1.0 mmol), *t*-BuHgCl (0.5 mmol), TEMPO (0.1 mmol) and in ter nal standard (0.05 mmol of biphenyl) were dis solved in 1 mL of nitro gen-purged dry sol vents. The solution was divided into four dry and ni tro gen-purged quartz tubes (0.25 mL in each tube) with each equipped with a rub ber sep tum. The tubes were ir ra di ated at 35-40 °C with a 100 W UV lamp placed about 20 cm from the re action tubes. The re action was monitored by GC or GCMS after the re action was photolyzed 1 hr and 2 hr. None of the S_H2' product was de tected by GC or GCMS and only the starting material was observed after photolysis.

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S_H2' mechanism; 2-Substituted allyl chloride; Single electron transfer; Radical addition; Trimethylsilyl radical; Photolysis; Competitive reaction.

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