1990

Free radical reactions of allylic and propargylic derivatives

Yuh-Wern Wu
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Free radical reactions of allylic and propargylic derivatives

by

Yuh-Wern Wu

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INTRODUCTION TO ORGANOMERCURIALS

The first organomercury compound, methylmercuric iodide, was reported by Edward Frankland in 1852.[1] Methylmercuric iodide was prepared by reacting mercury with methyl iodide under sun light. The mercury dialkyls were accidently discovered by Geroge Bowdler Buckton in 1858. He was trying to make methylmercuric cyanide by double decomposition, but the reaction took an unexpected turn and he isolated dimethylmercury as a heavy volatile liquid.[2] Mercuric acetate and benzene were found to react to give phenylmercuric acetate and the reaction was even more facile with suitably substituted benzenes, such as phenols, phenyl ethers, and derivatives of aniline.[3] This reaction made possible the preparation and study of a host of relatively non-toxic organomercurials. The chemistry of organomercuricals developed slowly, perhaps because of their toxicity, especially of the highly volatile dialkylmercurials (R_2Hg).[4] Although some organomercury compounds are very toxic, the vast majority of organomercury compounds are high melting crystalline solids and are easy to handle in the laboratory. Furthermore, organomercurials are easily obtained by a number of different synthetic methods,[5] and tolerate a variety of organic functional groups. They have been more broadly employed in organic syntheses, such as substitution reactions,[6,7] solvomercuration-demercuration reactions,[8,9,10] divalent carbon transfer reactions,[10, 11] and esterification reactions.[12,13]

In recent years, organomercury chemistry has attracted more interest of chemists as the development of organometallic chemistry has increased explosively. Organomercury halides, the most commonly used organomercurials, have been found to react by homolytic processes involving the corresponding alkyl radical , $R^{\bullet}$. The reaction of alkylmercury halides with sodium borohydride has been proven to be a radical

reaction.[14] An alkylmercury hydride, RHgH, is proposed to be involved in this reaction. The mechanism is shown in Scheme 1-1.

Scheme 1-1

$$RHgX + BH_4^- \longrightarrow RHgH$$

$$RHgH \longrightarrow R\bullet + Hg^\circ + H\bullet$$

$$R\bullet + RHgH \longrightarrow RH + RHg\bullet$$

$$RHg\bullet \longrightarrow R\bullet + Hg^\circ$$

The alkyl radicals generated by this method can be trapped by electron deficient olefins.[15] Giese and co-workers have studied the formation of C-C bonds by addition of free radicals, generated from alkylmercury halides and sodium borohydride, to electron poor alkenes.[16]

The reactions of alkylmercury halides with various anions were reported by Russell and co-workers.[17,18] They suggested these reactions proceed by an $S_{RN}1$ process as in Scheme 1-2.

Scheme 1-2

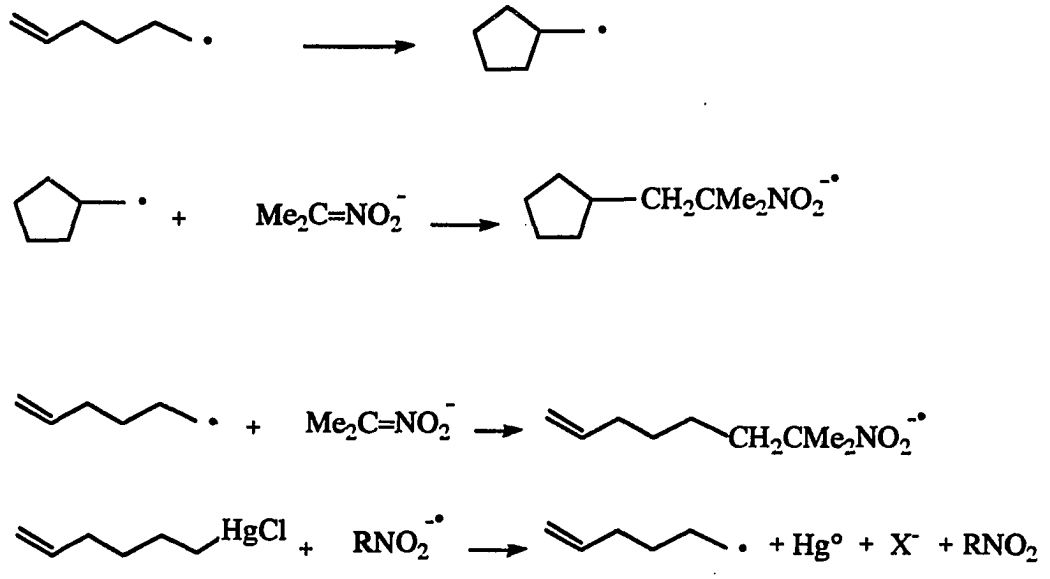
$$R\bullet + A^- \longrightarrow RA^{-\bullet}$$

$$RA^{-\bullet} + RHgX \longrightarrow RA + RHgX^{-\bullet}$$

$$RHgX^{-\bullet} \longrightarrow R\bullet + Hg^\circ + X^-$$

Evidence for the $S_{RN}1$ process involving radical anions and free radicals is provided by the cyclization of the 5-hexenyl radical (generated by electron transfer to 5-hexenylmercury chloride) to the cyclopentylcarbinyl radical in the presence of the anion of 2-nitropropene to form the radical anion of the adduct as shown in Scheme 1-3.[19] The reductions of alkylmercury halides by $LiAlH_4$ has also been suggested to proceed by an electron transfer chain mechanism of the $S_{RN}1$ type.[20]

Scheme 1-3



The reactions of alkylmercurials with diphenyl disulfide, diphenyl diselenide, diphenyl ditelluride, arylsulfonyl phenyl selenide, and benzenesulfonyl chloride have been shown to occur by the radical chain mechanism shown in Scheme 1-4.

Recently, Russell et al. have reported that organomercury halides can react with substituted alkenes and alkynes via a free radical addition-elimination mechanism.[21,22,23] The addition of an alkyl radical to a substrate, followed by the β-elimination of Q•, is shown in Scheme 1-5. The attack of Q• upon RHgX regenerates R• and continues the chain reaction.

Scheme 1-4

$$RHgX + QY \xrightarrow{h\upsilon} RY + QHgX$$

Q = PhS, PhSe, PhTe, $PhSO_2$, p-$CH_3C_6H_4SO_2$, CCl_3

Y = PhS, PhSe, PhTe, Cl, Br

$$RHgX + Q\bullet \longrightarrow R\bullet + QHgX$$

$$R\bullet + Q\text{-}Y \longrightarrow RY + Q\bullet$$

Scheme 1-5

$$R\bullet + R^1R^2C{=}CHQ \xrightarrow{\text{addition}} R^1R^2C^{\bullet}\text{-}CHQR$$

$$R^1R^2C^{\bullet}\text{-}CHQR \xrightarrow{\text{elimination}} R^1R^2C{=}CHR + Q\bullet$$

$$RHgX + Q\bullet \xrightarrow{S_H2} R\bullet + QHgX$$

or

$$RHgX + Q\bullet \xrightarrow{\text{E.T.}} R\bullet + Hg^{\circ} + Q^{+} + X^{-}$$

R = *t*-Bu, *i*-Pr, cyclohexyl, PhS

Q = I, HgCl, $PhSO_2$, *n*-Bu_3Sn, PhS

The photostimulated addition of alkylmercury chlorides to substituted ethylenes has been studied by Russell et al.[24] The reaction of alkylmercury halides with alkenes followed by sodium borohydride reduction yields the products shown in the following equation . The intermediate $RCH_2CH(HgCl)E$ involved in the free radical chain sequence has been trapped by formation of the corresponding iodide $RCH_2CH(I)Q$ from work-up of the product with iodine.

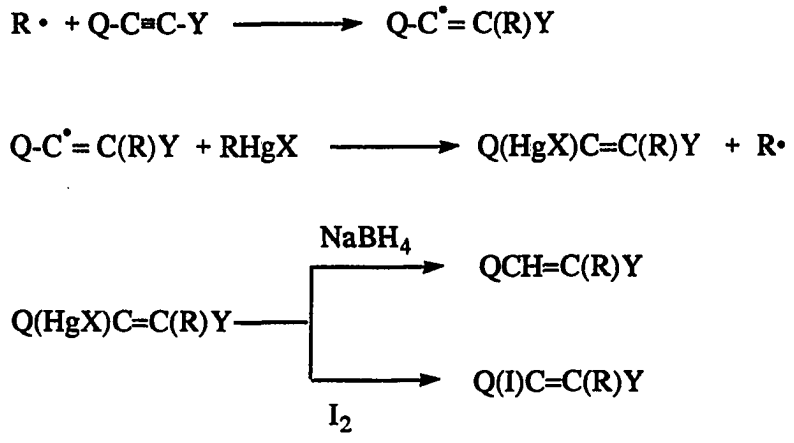
$$RHgCl + CH_2{=}CHE \longrightarrow RCH_2CH(HgCl)E \xrightarrow{NaBH_4} RCH_2CH_2E + Hg^\circ$$

$E = P(O)(OEt)_2$, $PhSO_2$

R = *t*-Bu, *i*-Pr, *n*-Bu, c-C_6H_{11}

Alkylmercury halides have been found to react with alkynes to form *E* and *Z* adducts as shown in Scheme 1-6. The adduct radical with Q = Ph is stabilized by electron delocalization into the phenyl ring.

Scheme 1-6



Q = Ph, COOEt, COMe

Y = H, COOEt

R = *tert*-Butyl

It is evident that organomercurials have been attracting more attention in recent years, particularly in the field of radical chemistry. The use of organomercury compounds in organic synthesis has interested many synthetic chemists and currently there is considerable interest in synthesis via radical processes.[25] The synthetic potential and application of organomercurials in organic synthesis will undoubtly increase in the future.

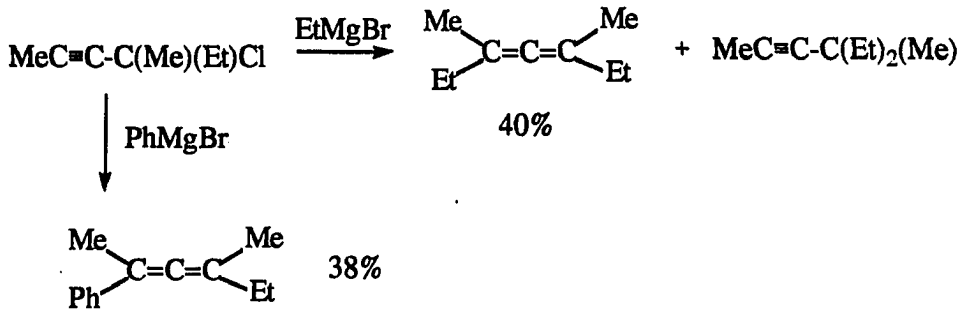
PART I. FREE RADICAL CHAIN REACTIONS OF PROPARGYL DERIVATIVES WITH ORGANOMERCURIALS

Introduction

Nucleophilic or organometallic additions to propargyl derivatives have become useful methods to synthesize allenic compounds. The reaction of propargyl halides with Grignard reagents has been reported by Gaudemar.[26] An S_N2' type of mechanism was proposed by Gaudemar while an allenic carbene intermediate was suggested by Serratosa.[27] However, the latter was strongly disputed by Brandsma and Arens[28] who suggested that the Grignard reagent had two functions, supplying the nucleophile and aiding in removal of the bromine. In practice, starting with propargyl bromide, terminal allenic hydrocarbons were obtained, mixed with the isomeric acetylene (produced by S_N2 substitution).

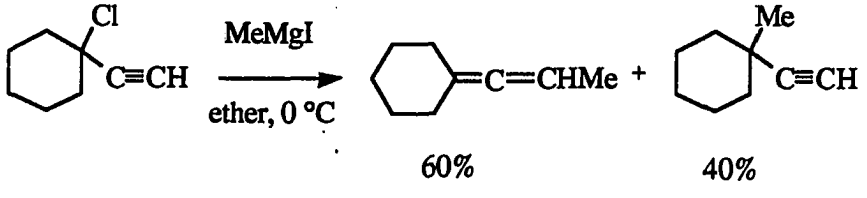
$$HC{\equiv}C\text{-}CH_2\text{-}Br + RMgBr \longrightarrow RHC{=}C{=}CH_2 + MgBr_2 + HC{\equiv}C\text{-}CH_2R$$

The reactions of alkylated derivatives of propargyl halides have been investigated extensively by Zakharova.[29] Jacobs and Meyers,[30(a)] and Macomer[30(b)] also found that substituted propargyl chlorides



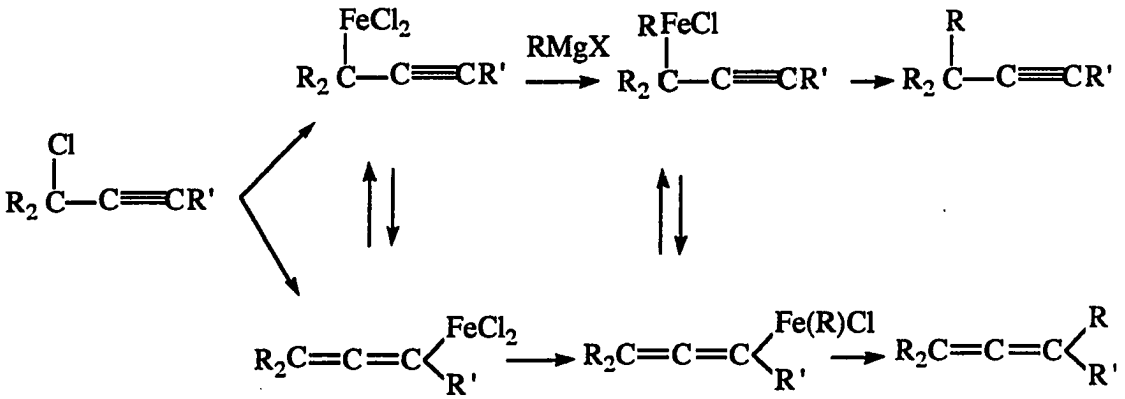
and Grignard reagents gave a mixture of acetylenic and allenic hydrocarbons. It appears that the allene/acetylene ratio decreases as the group attached to the acetylenic carbon becomes more branched, e.g., $Me_2(Cl)CC{\equiv}CBu\text{-}t$ gave 17% of the allene and 72% of the acetylene.

A detailed study of the reaction of (1-chlorocyclohexyl)acetylene and methylmagnesium iodide showed that the relative amounts of the allene and acetylene obtained depended on the temperature and the nature of the solvent.[31] The maximum yield of the allene was obtained at 0 °C with ether as the solvent, whereas refluxing THF gave the acetylene (95%).

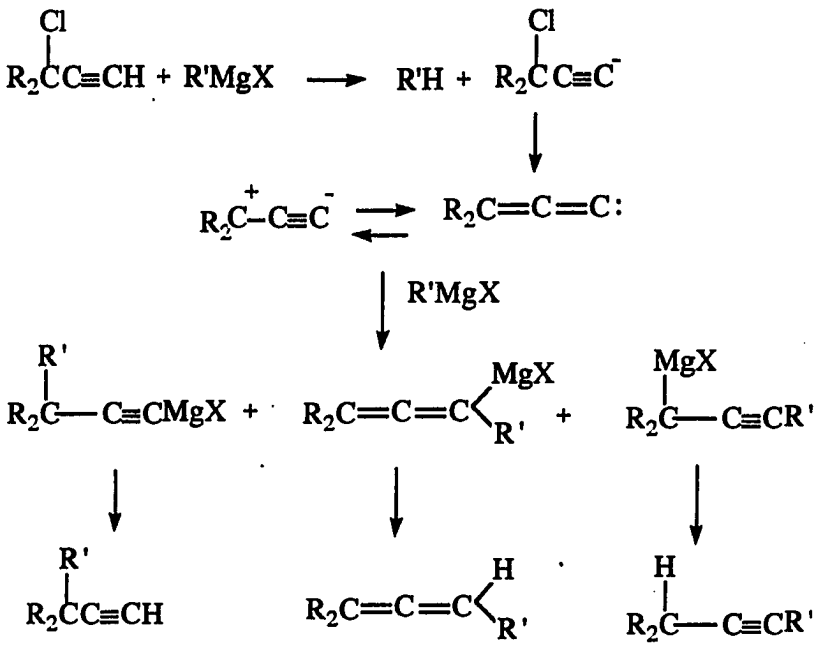


Pasto et al.[32] found that a mixture of an allene and alkyne was obtained in the reactions of Grignard reagents with propargyl derivatives in the absence of transition metal impurities. In the presence of a catalytic amount of iron(III) chloride, the same

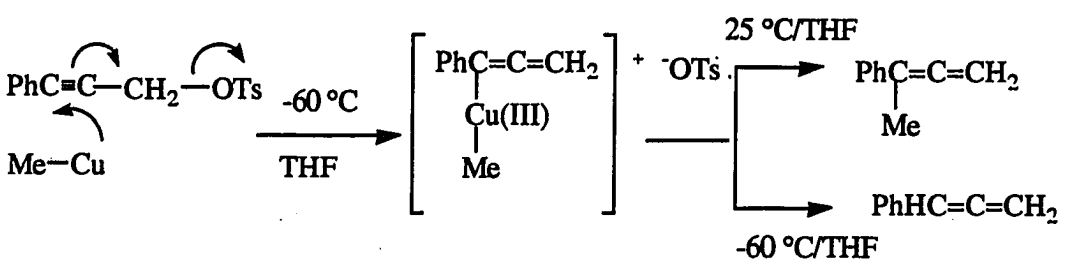
substrate gave only the allene in high yield. The mechanism of the catalyzed reaction suggested by Pasto involves a catalytic cycle with a low valency transition metal species.



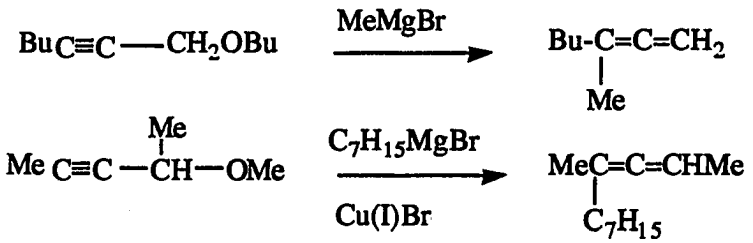
For the non-catalyzed reaction, a carbene intermediate was suggested. The carbene was postulated to be formed by proton abstraction of the acetylenic hydrogen atom by the Grignard reagent, followed by loss of chloride ion. Nucleophilic attack on the ion-carbene intermediate by a second molecule of the Grignard reagent leads to the mixture of the allene and the alkyne. However, no experimental evidence for the carbene intermediate was obtained.



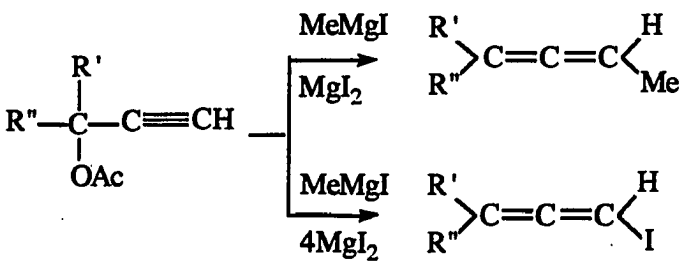
Brandsma et al. studied the reactions of the derivatives of propargyl tosylate with Grignard reagents in the presence of copper(I) bromide.[33] The allene obtained in these reactions is dependent upon the method of work-up. The reaction was thought to go through the copper intermediate shown since different methods of work-up gave either 1-methyl-1-phenylallene or 1-phenylallene.



Acetylenic ethers also react with Grignard reagents to give allenic hydrocarbons with a variety of alkyl substituents, e.g. 3-methylhepta-1,2-diene and 4-methyl-undeca-2,3-diene.[34,35]

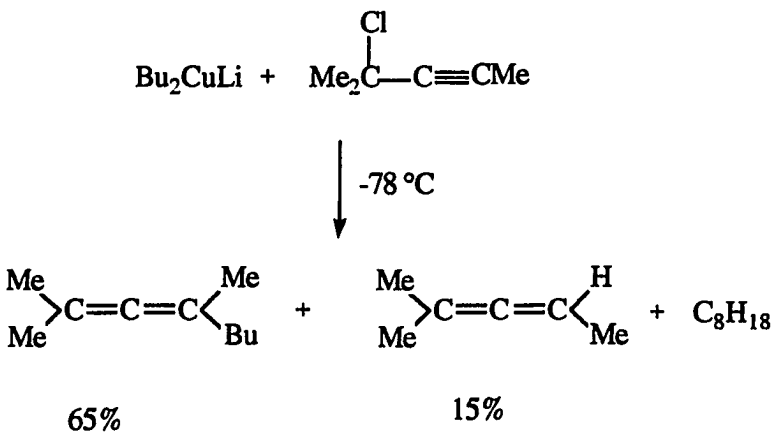


A detailed study with acetate as the leaving group by Gore et al.[36] has shown that the reaction of methylmagnesium iodide and tertiary propargyl acetates can lead to either methylallenes or iodoallenes as the main product, depending on the exact reaction conditions.



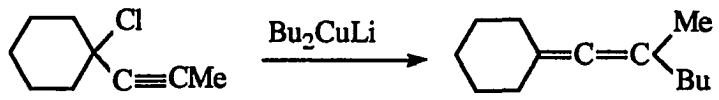
Phosphate as a leaving group has been reported[37] to give allenic hydrocarbons as the major product when propargyl derivatives are reacted with Grignard reagents in the presence of copper salts.

Organocuprate reagents has proven to be superior reagents for the formation of allenic compounds from propargyl derivatives.[38] Yields are above 60% for a variety of alkyl substituents, and it has been suggested that the propargyl halide reacts by a π-complex which decomposes to the allene. Reactions with Me_2CuLi were carried out at -5 °C, with Et_2CuLi at -30 °C, and with *n*-Bu_2CuLi at -60 °C. The π-complex mechanism was supported by Pasto et al.[39] who also found that some halides gave a mixture of alkylated and non-alkylated allenes. Coupling of the alkyl groups attached to copper also occurred with Bu_2CuLi.

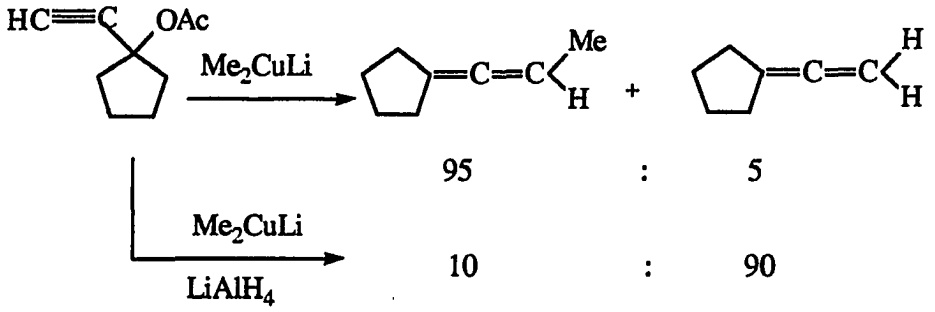


The reaction at 0 °C was very fast, but the yield of alkylated allene was lower. On the other hand, the reaction of 1-prop-1-ynylcyclohexyl chloride with the same cuprate gave only the alkylated allene. Apparently the decomposition of the π-complex to give

alkylated or non-alkylated allene depends both on the temperature and on the nature of the alkyl groups attached to the triple bond.



The reactions of propargylic acetates with dialkylcuprates has been studied in a series of papers,[40] and alkylated or non-alkylated allenic hydrocarbons can be produced by varying the reaction conditions. For instance, starting with the (1-acetoxycyclopentyl) acetylene and dimethylcuprate, an alkylated allene is produced as the major product at -10 °C, but non-alkylated product at -75 °C, when lithium aluminium hydride was added after 1 hour.[40c]

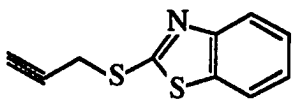


Crabbe and co-workers in a mechanistic study of this reaction[40b] showed by using $(CD_3)_2CuLi$ that in the formation of non-alkylated allene the entering hydrogen did not

originate from the organocuprate, and further, for the alkylated allene that the reaction was at least partly stereospecific; a covalent organocopper intermediate was suggested.

Organotin hydrides are useful reagents for the reduction of organic compounds such as halides, aldehydes, ketones, isocyanates, and isothiocyanates.[41] They were found to add to carbon-carbon double or triple bond. Certain of these reactions can proceed by free radical mechanisms in which organic radicals are intermediates. Hydrogen atom transfers from organotin hydride to these radicals is a very fast process.

Tri-*n*-butylstannyl radical is known to add to mutiple bonds reversibly.[42] Uneo and Okawara have reported the desulfurizative stannylation of allylic or propargylic sulfides via an S_H2' process.[43] Thus, tri-*n*-butylstannyl radical generated from azobisisobutyronitrile and tri-*n*-butyltin hydride reacted with 2-(propargylthio)benzothiazole to give tri-*n*-butylstanylallene in high yield.

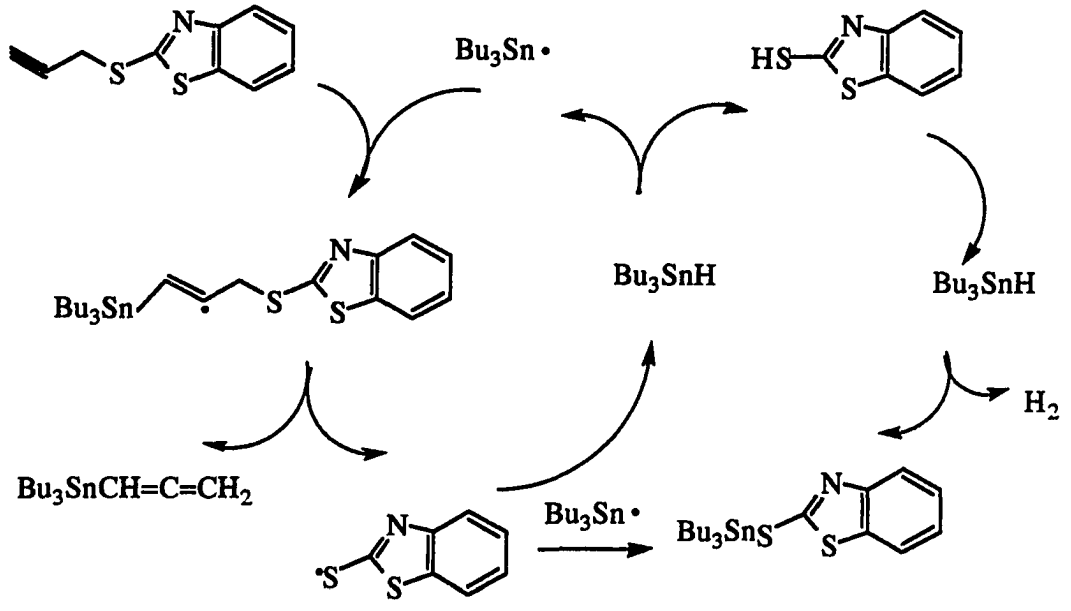


+ *n*-Bu_3SnH $\xrightarrow[\text{or h}\upsilon]{\text{AIBN, 100 °C}}$ $Bu_3SnCH{=}C{=}CH_2$

90-93%

The mechanism as shown in Scheme 1-7 involves the addition of tri-*n*-butylstannyl radical at the terminal carbon atom of the multiple bond. The resulting radical then eliminates the benzothiazoylthiyl radical to form the allene product. The thiyl radical abstracts hydrogen atom from the tin hydride to give the thiol and tri-*n*-butylstannyl radical which continues the chain.

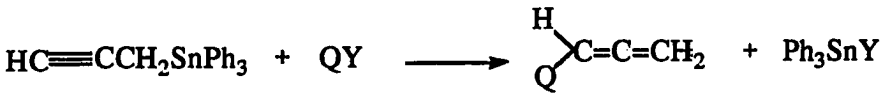
Scheme 1-7



Baldwin et al. have studied the substitution reaction of triphenylpropargyltin with alkyl halides to provide terminal allene in moderate yields.[44]

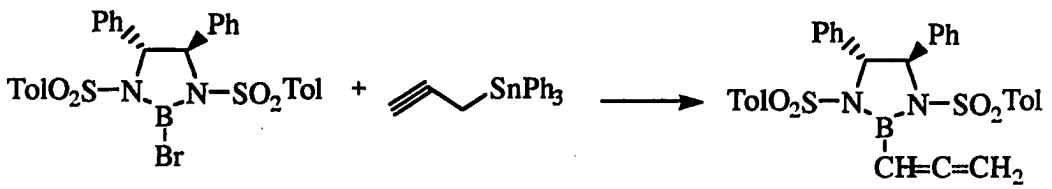
$$RX + HC{\equiv}CCH_2SnPh_3 \xrightarrow[AIBN,\ 80\ ^\circ C]{PhH} RCH{=}C{=}CH_2 + Ph_3SnX$$

Recently, Russell and Herold have found that the triphenylpropargyltin can undergo free radical substitution reactions with heteroatom-centered radicals leading to allene products.[45]



QY = PhSSPh, $PhCH_2SSCH_2Ph$, PhSeSePh, $PhSO_2Cl$, *n*-$PrSO_2Cl$, CCl_3SO_2Cl.

Corey et al. used the (*R*,*R*)-bromoborane reagent shown to react with triphenylpropargyltin in dry dichloromethane. The allenylborane was obtained in high yield.[46]



The photostimulated addition of alkyl radicals derived from alkylmercury halides to propargyl derivatives has never been reported. The following section will present reactions of propargyl derivatives with organomercurials as shown in the following equation.

A discussion concerning the mechanism of the reaction of *tert*-butylmercury halide with propargyl derivatives will be presented. Some other possible sources of *tert*-butyl radicals will also be considered.

Results and Discussion

Reactions proceeding by the S_H2' process

Propargyl chloride was allowed to react with excess *tert*-butylmercury chloride in dimethyl sulfoxide (DMSO) under sunlamp irradiation. The reaction was found to proceed according to equation (1-1).

$$HC{\equiv}CCH_2Cl + t\text{-BuHgCl} \xrightarrow{h\upsilon} H_2C{=}C{=}CH\,Bu\text{-}t + HgCl_2 \quad (1\text{-}1)$$

After photolysis about 7 hours, this reaction gave a low yield of product, 4,4-dimethyl-1,2-pentadiene. However, in the presence of NaI, the yield increased to 64% with 5 equiv of *t*-BuHgCl. DMSO was used as the solvent, because the reaction seemed to proceed well and all starting materials and products were readily soluble. After the reaction, DMSO and the mercury(II) salt were easily removed by washing the reaction mixture with water while the organic products were extracted with ether or dichloromethane. The extract was then washed with an aqueous solution of sodium thiosulfate to remove the remaining alkylmercury chloride. The mixture was concentrated and analyzed by GLC, GCMS and NMR spectroscopy. The product was compared with the authentic compound by proton NMR spectroscopy, GLC and GCMS. The yields

were determined by quantitative H^1 NMR spectroscopy or by GLC using biphenyl or toluene as the internal standard.

Benzene was also employed as the reaction medium, but it was found that the reaction in this medium occurred sluggishly and the yield was low. When benzene was used, a white solid precipitated during the reaction. The low solubility of alkylmercurials was also a problem in benzene.

Russell and Ngoviwatchai had found that the allylic derivatives (include halides, sulfide, sulfone) reacted with *t*-BuHgCl by the S_H2' process as shown in Scheme 1-8.[47]

Scheme 1-8

$$R\bullet + H_2C{=}CHCH_2A \longrightarrow RCH_2\dot{C}HCH_2A \quad (1\text{-}2)$$

$$RCH_2\dot{C}HCH_2A \longrightarrow RCH_2CH{=}CH_2 + A\bullet \quad (1\text{-}3)$$

$$A\bullet + RHgCl \longrightarrow AHgCl + R\bullet \quad (1\text{-}4)$$

The alkyl radical added at the terminal carbon of the double bond to form an intermediate adduct radical which underwent β-elimination of the leaving group A• in a chain process.

Table 1-1 summarizs the results of the reactions of propargyl derivatives and *t*-BuHgCl. A 5-fold excess of *t*-BuHgCl was employed and the reactions were carried out in DMSO under sunlamp irradiation. The reactions were usually irradiated for 7 h, but no attempt was made to determine the exact time needed to optimize the yield, since *t*-$BuCH{=}C{=}CH_2$ appeared to be stable under the reaction conditions.

Table 1-1. Reactions of Propargyl Derivatives with *t*-BuHgCl at 35-45 °C in Me_2SO

Substrate(mmol)	Mercurial(equiv)	Conditions[a]	% Product [b]
$HC{\equiv}CCH_2Cl$ (0.1)	*t*-BuHgCl (5)	7h	20
$HC{\equiv}CCH_2Cl$ (0.1)	*t*-BuHgCl (5)	7h, 5 equiv NaI	64
$HC{\equiv}CCH_2Cl$ (0.1)	*t*-BuHgI (5)	7h	39
$HC{\equiv}CCH_2Cl$ (0.1)	*t*-BuHgI (5)	6h, 5 equiv NaI	73
HC≡CCH(Me)Cl(0.1)	*t*-BuHgCl (5)	7h	0[c]
$HC{\equiv}CCH_2Br$ (0.1)	*t*-BuHgCl (5)	7h	6
$HC{\equiv}CCH_2Br$ (0.1)	*t*-BuHgCl (5)	7h, 5 equiv NaI	14
$HC{\equiv}CCH_2Br$ (0.1)	*t*-BuHgI (5)	7h	7
$HC{\equiv}CCH_2Br$ (0.1)	*t*-BuHgI (5)	4h, 5 equiv NaI	0
$HC{\equiv}CCH_2SPh$ (0.1)	*t*-BuHgCl (5)	25h	< 10
$HC{\equiv}CCH_2SPh$ (0.1)	*t*-BuHgCl (5)	7h, 5 equiv NaI	26
$HC{\equiv}CCH_2SO_2Ph$ (0.1)	*t*-BuHgCl (5)	23h	< 10

[a] Substrate (0.1 M) and mercurial in nitrogen-purged Me_2SO or DMSO-d_6 were irradiated with a 275 W sunlamp ca. 20 cm from the reaction flask.

[b] The product is *t*-$BuC{=}C{=}CH_2$. The yield was determined by ^1H NMR.

[c] 27% recovery of HC≡CCH(Me)Cl; in the presence of 5 equiv NaI, the substitution product was not observed and 62% of HC≡CCH(Me)Cl was recovered.

Table 1-2 reports data for the analogous S_H2' reaction of allylic derivatives with *t*-BuHgCl. The yields are higher and the reactions faster for the allylic derivatives.

Table 1-2. Reactions of Allyl Derivatives with *t*-BuHgCl at 35-45 °C in Me_2SO

Substrate(mmol)	Mercurial(equiv)	Conditions[a]	% Product [b]
H_2C=$CHCH_2Cl$(0.1)	*t*-BuHgCl (5)	4.5h	92
H_2C=$CHCH_2Cl$(0.1)	*t*-BuHgCl (5)	3h, 5 equiv NaI	100
H_2C=$CHCH_2Cl$(0.1)	*t*-BuHgCl (5)	1h	65
H_2C=$C(Me)CH_2Cl$(0.1)	*t*-BuHgCl (5)	1h	57[c]
		2h	63[c]
H_2C=$CHCH_2Br$(0.1)	*t*-BuHgCl (5)	1h	62
H_2C=$CHCH_2I$ (0.1)	*t*-BuHgCl (5)	1h	45

[a] Substrate (0.1 M) and mercurial in nitrogen-purged Me_2SO or DMSO-d_6 were irradiated with a 275 W sunlamp ca. 20 cm from the reaction flask.

[b] The product is *t*-$BuCH_2CH$=CH_2. The yield was determined by ^1H NMR.

[c] The product is *t*-$BuCH_2C(Me)$=CH_2.

The substitution reaction (Eq. 1-1) appears to proceed by a radical chain process since no reaction was observed in the dark. Furthermore, the reaction was completely inhibited by di-*tert*-butyl nitroxide (DTBN), a radical chain inhibitor. We believe that the mechanism involves radical addition-elimination as outlined in Scheme 1-9.

Scheme 1-9

Initiation[48]

$$RHgCl \xrightarrow{h\upsilon} R\bullet + \bullet HgCl \xrightarrow{RHgCl} R\bullet + HgCl_2 + Hg^{\circ}$$

Propagation

$$HC{\equiv}CCH_2A + R\bullet \longrightarrow RCH{=}\dot{C}\text{-}CH_2A$$

1

$$RCH{=}\dot{C}\text{-}CH_2A \longrightarrow RCH{=}C{=}CH_2 + A\bullet$$

1

$$A\bullet + RHgCl \longrightarrow AHgCl + R\bullet$$

A = Cl, SPh, SO_2Ph.

The initiation step arises from the photolysis of the alkylmercurial. In the propagation step, the alkyl radical attacks the terminal position of the triple bond to give **1**. The resulting radical **1** undergoes β-elimination to give the substitution product and

radical A•. The radical A• reacts with the alkylmercurial chloride to give AHgCl and an alkyl radical which continues the chain.

In a direct competition of allyl and propargyl chloride for *t*-Bu•, it was found that the allyl system was about 10 times as reactive as the propargyl system. This reactivity difference is reflected in the yield of *t*-$BuCH_2CH{=}CH_2$ and *t*-$BuCH{=}C{=}CH_2$ reported in Table 1-1 and Table 1-2. Because of the lower reactivity in the addition of the alkyl radical, the propargyl system is particularly vulnerable to reaction 1-5 which diverts the radical and terminates the chain sequence of Scheme 1-9.

$$HC{\equiv}CCH_2X + R\bullet \longrightarrow HC{\equiv}CCH_2\bullet + RX \qquad (1\text{-}5)$$

X = I, Br

Under comparable conditions, the yields of substitution products decrease from the allyl to the propargyl system and as X is changed from Cl to Br to I. Alkylation at the allylic or propargylic carbon also increased the importance of reaction 1-5 and the substitution product was not observed for HC≡CCH(Me)Cl. With HC≡CCH(Me)OTs where halogen atom transfer was not a problem, a 38% yield of *t*-BuCH=C=CH(Me) was observed in 7h with 5 equiv of *t*-BuHgCl.

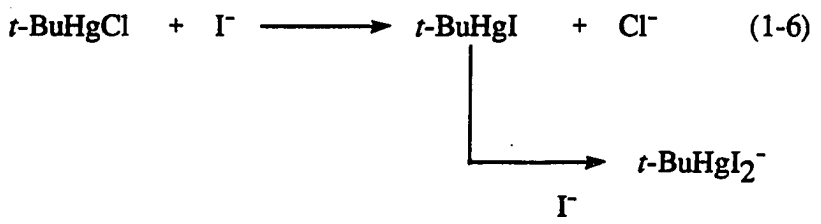
Iodide ion promoted reaction of *t*-BuHgCl and propargyl chloride

The rate and yield of the reaction of propargyl and allyl chloride with *t*-BuHgCl in DMSO were increased in the presence of NaI. This may reflect that *t*-BuHgCl reacts with I^- to form *t*-BuHgI (or *t*-$BuHgI_2^-$) (Eq. 1-6) which increases the rate of photoinitiation or that there is an electron transfer between I^- (or *t*-$BuHgI_2^-$) and the

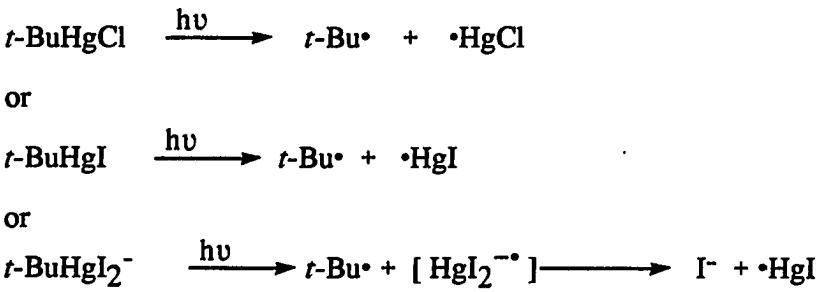
adduct radical 2 (Eq. 1-8). A possible mechanism for the reaction of propargyl chloride with the alkylmercury halide in the presence of NaI is shown in Scheme 1-10.

Scheme 1-10

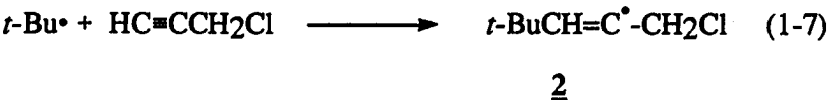
Exchange and Complexation



Photoinitiation



Propagation



2

$$t\text{-BuCH=C}^{\bullet}\text{-CH}_2\text{Cl} \longrightarrow t\text{-BuCH=C=CH}_2 + \text{Cl}^{\bullet}$$

2

$$\text{Cl}^{\bullet} + t\text{-BuHgX} \longrightarrow t\text{-Bu}^{\bullet} + \text{HgClX}$$

Electron Transfer

$$t\text{-BuCH=C}^{\bullet}\text{-CH}_2\text{Cl} + \text{I}^{-} \xrightarrow{\text{E.T.}} t\text{-BuCH=C}^{-}\text{-CH}_2\text{Cl} + \text{I}^{\bullet} \quad (1\text{-}8)$$

2 **3**

or

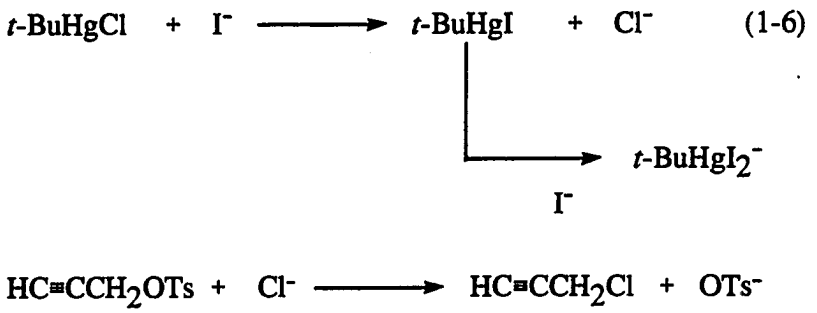
$$t\text{-BuCH=C}^{\bullet}\text{-CH}_2\text{Cl} + t\text{-BuHgI}_2^{-} \xrightarrow{\text{E.T.}} \underline{3} + \text{HgI}_2 + t\text{-Bu}^{\bullet} \quad (1\text{-}9)$$

β-Elimination

$$t\text{-BuCH=C}^{-}\text{-CH}_2\text{Cl} \xrightarrow{\text{fast}} \text{t-BuCH=C=CH}_2 + \text{Cl}^{-} \quad (1\text{-}10)$$

The evidence for formation of *tert*-butylmercury iodide (or the ate complex) is that propargyl chloride was found in the reaction of propargyl tosylate with *t*-BuHgCl in the presence of NaI before the photolysis. This indicates that I^- replaced the chloride from the *t*-BuHgCl to produce *t*-BuHgI (or *t*-$BuHgI_2^-$) and Cl^- (Eq. 1-6). The chloride ion ,

which is a strong nucleophile in DMSO, then attacked propargyl tosylate to form propargyl chloride and OTs^-.



Alkylmercurates were first reported by Emeleus and Lagowski[49] in 1959. A short time after Emeleus and Lagowski's report, Barbieri et al., Rizzardi and Pietropalo, and Stocco et al. published several reports[50] on the formation of mercurates, $[RHgX_n]^{1-n}$ (where n=2,3), of ethyl and 2-butyl mercurials, where X=Cl, Br, and SCN. In 50% aqueous methanol, they observed that $[RHgX_2]^-$ was the favored mercurate while $[RHgX_3]^{2-}$ was favored in aqueous solution.

The reactions of propargyl chloride with *t*-BuHgCl in the presence of various amounts of NaI or NH_4Cl are summarized in Table 1-3. It was found that increasing the mole ratio of NaI /*t*-BuHgCl increased the yield of the allene, but only up to a NaI : *t*-BuHgCl ratio of 2 : 1. Presumedly, if there had been an electron transfer between the adduct radical 2 and I^- (Eq. 1-8), increasing the mole ratio of NaI /*t*-BuHgCl still further would increase the yield and rate of allene formation. However, this was not observed.

The yield of the substitution reaction of propargyl chloride with *t*-BuHgCl also increased in the presence of Cl^-. However, electron transfer between adduct radical 2 and Cl^- would not be expected. The yield of the substitution product did not increase siginificantly when the mole ratio of Cl^- /*t*-BuHgCl exceeded 1. The possibility of formation of *t*-$BuHgCl_2^-$ from *t*-BuHgCl and Cl^- was indicated by these results; this ate complex might increase the photoinitiation rate or there might be an electron transfer between *t*-$BuHgCl_2^-$ and adduct radical 2.

Russell and co-workers[51] have found that iodide ion can promote the free radical reactions of isopropylmercury bromide with a rate enhancement in the order of 10^4. The reaction involves electron transfer from *i*-$PrHgI_2^-$ to the trichloromethyl radical in a long kinetic chain process. In the presence of NH_4I, the reaction yields CCl_3H and *i*-PrBr in a 1:1 ratio, consistent with reaction 1-12 and 1-13.

$$CCl_3\bullet + i\text{-}PrHgI_2^- \longrightarrow i\text{-}Pr\bullet + CCl_3^- + HgI_2 \qquad (1\text{-}12)$$

$$i\text{-}Pr\bullet + BrCCl_3 \longrightarrow i\text{-}PrBr + CCl_3\bullet \qquad (1\text{-}13)$$

Russell and co-workers[51] also found that the thermal production of *t*-Bu• from *t*-BuHgX at 60 °C in DMSO as measured by ESR spin trapping with *tert*-butylphenylnitrone is a first order process with k increasing from 3.5×10^{-9} s^{-1} for X = Cl to 1.4×10^{-7} s^{-1} with X= I and 2.0×10^{-5} s^{-1} with X= *t*-Bu. In the presence of 2 equiv of I^-, the thermolysis of 0.1 M *t*-BuHgX at. 60 °C is accelerated 200-fold for

X= Cl and 10-fold for X= I, with the formation of *t*-Bu• occurring primarily by a process first order in both *t*-BuHgI and I^-.

From the above discussions, an electron transfer between I^- and the adduct radical 2 (Eq. 1-8) is excluded in the reaction of propargyl chloride and *t*-BuHgCl in the presence of NaI. There is little evidence to support an electron transfer reaction between *t*-$BuHgX_2^-$ and adduct radical 2 (Eq. 1-9). (This will be discussed further in Part III.) It seems reasonable that the reaction of propargyl chloride with *t*-BuHgCl in the presence or absence of I^- proceeds via the S_H2' mechanism. Possibly the increased rate and yield in the presence of I^- can be explained by the increased rate of the initiation reaction resulting from the ate-complex, *t*-$BuHgX_2^-$. However, another aspect of the reaction may be involved. The S_H2' reaction of propargyl chloride leads to the formation of the chlorine atom. The chlorine atom is a very reactive species which can abstract hydrogen atom from the solvent or add to multiple bonds and the new radicals produced may not continue the chain. Possibly the chlorine atom is too reactive a species to participate in a long kinetic chain process of the S_H2'-type. In the presence of I^-, or $RHgX_2^-$, the chlorine atom would be expected readily from I• or R• ($Cl• + RHgX_2^- \longrightarrow Cl^- + R• + HgX_2$). The effect of I^- may thus be connected with the improved kinetic chain length which would result if the chlorine atom was rapidly replaced by a more efficient chain propagating species, i.e. I• or R•.

Table 1-3. Reactions of propargyl chloride with *t*-BuHgCl in the presence of different equiv NaI or NH_4Cl[a]

equiv *t*-BuHgCl	equiv NaI	equiv NH_4Cl	%product[b]
5	-	-	20
5	5	-	64)
2.5	2.5	-	47
2.5	5	-	61
2	2	-	27
2	4	-	40
2	6	-	39
5	-	1	32
5	-	5	44
5	-	10	48
5 (*t*-BuHgI)	-	-	39
5 (*t*-BuHgI)	5		71

[a] Substrate (0.1 M) and mercurial in nitrogen-purged DMSO-d_6 were irradiated with a 275 W sunlamp ca. 20 cm from the reaction flask.

[b] All the reactions were irradiated about 7 hours under a sunlamp and 4,4-dimethyl-1,2-pentadiene was the product. The yield was determined by ^1H NMR .

Substitution reactions involving intermediate organomercurials

Table 1-4 summarizes the substitution yields for the propargyl system which are presumed to proceed via Scheme 1-11 and to involve intermediate **4**. It is recognized that oxygen-centered radicals are not readily eliminated in reaction 1-3, and it seems unlikely that these substitutions could occur via Scheme 1-8 (page 19). In fact, for the allyl system with the substituents A' = OAc, OH, OPh, or $OSiMe_3$, Russell and co-workers[47] have found that intermediates **5** can be detected by ^1H NMR spectroscopy (Scheme 1-12). In the propargyl system, intermediate **4**, as a mixture of *E* and *Z* isomers, was detected by ^1H NMR spectroscopy with A' = OAc or OBz.

Scheme 1-11

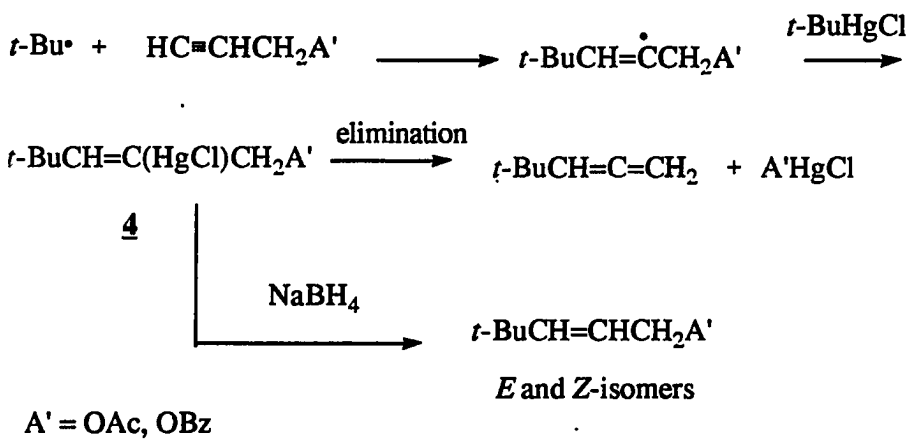


Table 1-4. Reaction of Oxy-Substituted $HC{\equiv}CCH_2A'$ with *t*-BuHgCl in DMSO[a]

A'[b]	equiv *t*-BuHgCl	equiv NaI	time, h	product	% yield[c]
OTs	5	0	7	*t*-BuCH=C=CH_2,	70%
OTs	5	5	7	*t*-BuCH=C=CH_2,	36%
OTs	5[d]	5	4	*t*-BuCH=C=CH_2,	5%
$OP(O)(OEt)_2$	5	5	7	*t*-BuCH=C=CH_2,	50%
OAc	5	0	7	4(A' = OAc, E/Z = 2),	62%
O_2CPh	5	0	48	4(A' = O_2CPh),	95%
O_2CPh	5	5	7	*t*-BuCH=C=CH_2,	25%

[a] Substrates and 0.1 M *t*-BuHgCl in DMSO-d_6 with photolysis by a 275 W sunlamp ca. 20 cm from the reaction vessel.

[b] OTs = p-toluenesulfonate.

[c] ^1H NMR spectroscopic yields relative to an internal standard.

[d] *t*-BuHgI.

Scheme 1-12

$$t\text{-Bu}^{\bullet} + H_2C{=}CHCH_2A' \longrightarrow t\text{-BuCH}_2\dot{C}HCH_2A' \xrightarrow{t\text{-BuHgCl}}$$

$$t\text{-BuCH}_2CH(HgCl)CH_2A' \xrightarrow{I^- \text{ or } CN^-} t\text{-BuCH}_2CH{=}CH_2$$

5

A' = OAc, OH, OPh, $OSiMe_3$

Winstein and Smith [52] have reported that dimethyl sulfoxide was a nucleophilic ionizing solvent for reactions with alkyl halides or arenesulfonates. The action of DMSO on a simple alkyl halide gives rise to two different types of derivatives, both with the proper elementary analysis for 1:1 adducts of RX and DMSO, which are O- and S-alkyl derivatives.

The reaction of benzoyl chloride with DMSO, shown in the following equation, was reported by Thea and Cevasco.[53]

$$ArCOCl + OS(Me)_2 \longrightarrow ArCOO\text{-}S^+(Me)_2 \xrightarrow{\text{base}} ArCOCH_2SOCH_3$$

Russell and co-workers also have found that DMSO reacts with allyl derivatives to form an allyl sulfoxonium salt.[47] Allyl iodide formed a single sulfoxonium salt

$$CH_2{=}CH\text{-}CH_2\text{-}A + Me_2SO \longrightarrow CH_2{=}CH\text{-}CH_2\text{-}(SMe_2O^+) + A^-$$

A= I, $PhSO_3$, OTs.

$[CH_2{=}CH\text{-}CH_2\text{-}(SMe_2O^+)]$[47] in a process which was greatly accelerated in the dark by the presence of *t*-BuHgCl.[47] It was observed that the photostimulated formation of *t*-$BuCH_2CH{=}CH_2$ was not actually observed until the iodide had been completely converted to the sulfoxonium salt. The substitution reaction of allyl iodide thus involves the addition of *t*-Bu• to the sulfoxonium salt to yield *t*-$BuCH_2C^{\bullet}HCH_2(SMe_2O)^+$. It seems unlikely that the species $SMe_2O^{+\bullet}$ would be eliminated and instead the process of Scheme 1-12 is presumed to occur (A' = SMe_2O^+), where A'HgCl = $Me_2SO\cdots{}^+HgCl$. The elimination reaction in this case must occur rapidly since there was no evidence from ^1H NMR spectroscopy for an intermediate organomercurial. The possibility of sulfoxonium salt formation from the propargylic halides in DMSO was investigated by ^1H NMR spectroscopy in DMSO-d_6. Propargyl iodide failed to form a salt at an appreciable rate and *t*-$BuCH{=}C{=}CH_2$ was not observed upon photolysis in the presence of *t*-BuHgCl, presumably because of the dominance of reaction 1-5. Intermediate 5 (A' = OAc) was formed from allyl acetate in 74% yield during a 2-h period of photolysis, but in the presence of excess I^-, intermediate 5 was not detected and a 64% yield of *t*-$BuCH_2CH{=}CH_2$ was formed. Intermediate 5 from allyl acetate was converted to *t*-$BuCH_2CH{=}CH_2$ slowly in the dark at 45 °C and rapidly upon treatment with I^- or CN^- in DMSO. Apparently, the elimination of the elements HgCl and OAc can occur by an E_2-type reaction initiated by the attack of a nucleophile upon the mercury atom. In a similar fashion, intermediate 5 with A' = OPh, $OSiMe_3$, or OH was obtained only in the absence of added iodide ion.[47] Analogous behavior was

observed in the reactions of $HC{\equiv}CCH_2A'$ with A' = OAc, OBz in the absence of I^-. A mixture of intermediate **4** (*E* and *Z* isomers) was detected by ^1H NMR spectroscopy in the absence of I^-. However, intermediate **4** was not detected in the presence of I^-. Apparently, the elimination of the elements HgCl and OAc (or OBz) can occur by an E_2-type reaction. Reduction of the intermediate **4** with $NaBH_4$ yielded the expected *t*-$BuCH{=}CHCH_2A'$ (*E* and *Z* isomers) with A' = OAc, OBz.

Propargyl tosylate reacted with *t*-BuHgCl upon photolysis in DMSO solution to form *t*-$BuCH{=}C{=}CH_2$. Intermediate **4** could not be detected, and in a ^1H NMR spectroscopy experiment in DMSO-d_6, the initial rate of formation of the allene was almost equal to the rate of disappearance of propargyl tosylate (Figure 1-1). Apparently, intermediate **4** with A'= OTs undergoes a very rapid elimination. (This will be discussed further in Part III.) The substitution reaction was inhibited by (*t*-$Bu)_2NO^{\bullet}$, and from the inhibition period an initial kinetic chain length of > 300 was calculated (0.1 M $HC{\equiv}CCH_2OTs$, 0.5 M *t*-BuHgCl) (see Part II). Iodide ion inhibited the reaction (Table 1-4) apparently by forming the propargyl iodide which could enter into the chain-terminating halogen atom transfer reaction (reaction 1-5) (page 23). Propargyl tosylate in DMSO is slowly converted into the sulfoxonium salt in the presence or absence of *t*-BuHgCl in the dark. The mixture, which was monitored periodically by ^1H NMR spectroscopy, showed two kinds of sulfoxonium intermediates which are presumably O- and S-alkyl derivatives as shown in Scheme 1-13. The results are shown in the Table 1-5.

It seems reasonable to assume that chemical shifts of ^1H NMR spectroscopy of O-propargyl sulfoxonium salt (**I**) will shift to downfield and S-propargyl sulfoxonium salt (**II**) will shift to upfield. The chemical shifts of these compounds are listed in Table 1-7 (page 50). The yields of sulfoxonium salts shown in Table 1-5 are consistent with the

Curve A : disappearance of propargyl tosylate

Curve B : formation of *tert*-butylallene

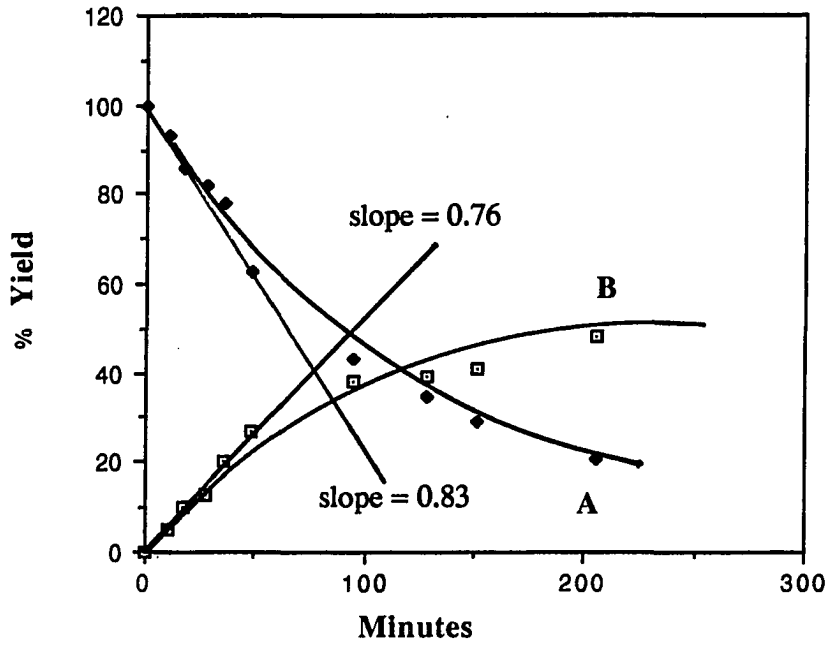
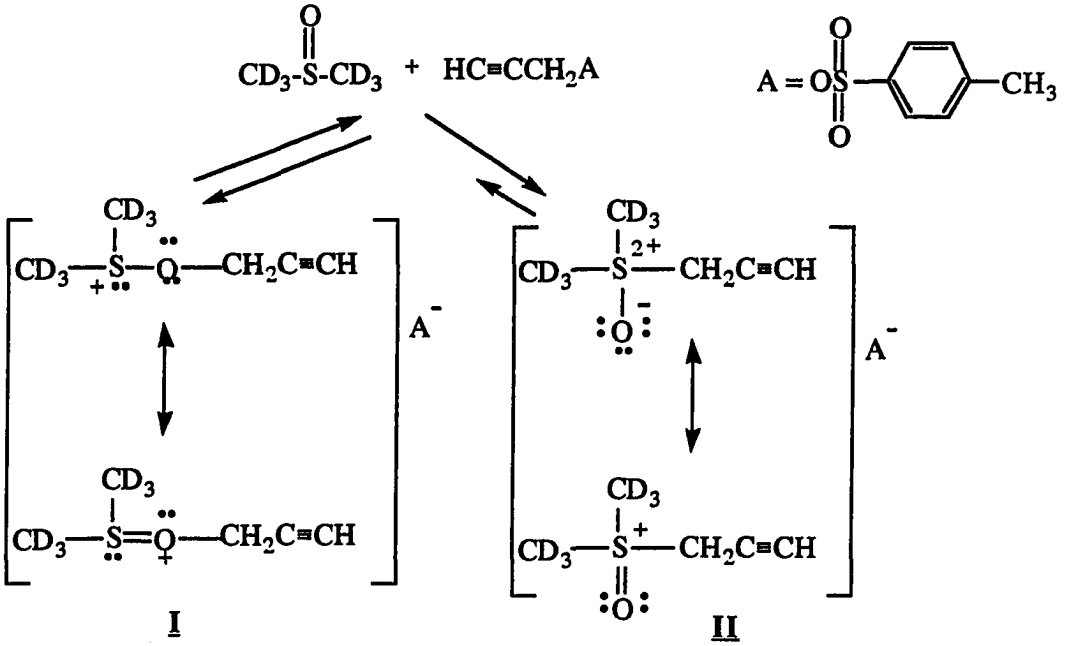


Figure 1-1. The rate of formation of *tert*-butylallene vs. the rate of disappearance of propargyl tosylate

S-propargyl sulfoxonium salt (II) being the thermodynamic product and the O-propargyl sulfoxonium salt (I) the kinetic product.[52]

Scheme 1-13



From Table 1-5, it is apparently that the rate of reaction of propargyl tosylate with DMSO is quite slow. The S-alkyl sulfoxonium salt is the thermodynamic product, while the O-alkyl sulfoxonium salt is the kinetic product. After the formation of the propargyl sulfoxonium salt, the addition of *t*-BuHgCl to the mixture under photolysis gave a low yield (10-15%) of 4,4-dimethyl-1,2-pentadiene. The propargyl sulfoxonium salts was not involved in the photostimulated reaction of propargyl tosylate with *t*-BuHgCl. On the other hand, the propargyl diethyl phosphate also gave a clean substitution reaction upon photolysis with *t*-BuHgCl in DMSO, and the iodide retardation observed with propargyl tosylate was not found for the phosphate.

Table 1-5. Reactions of propargyl tosylate with DMSO with or without mercurial

reaction conditions[a]	$HC{\equiv}CCH_2Q^b$	$HC{\equiv}CCH_2Q'^c$	$HC{\equiv}CCH_2Cl$
hυ 4h	22%		
hυ 8h	25%		
hυ 23h	44%	6%	
hυ 27h	45%	9%	
hυ 44h	32%	22%	
5 equiv *t*-BuHgCl dark, 35-45 °C, 4h	13%		
5 equiv *t*-BuHgCl dark, 35-45 °C, 8h	9%	15%	1%
5 equiv *t*-BuHgCl dark, 35-45 °C, 23h		40%	4%
5 equiv *t*-BuHgCl dark, 35-45 °C, 27h		45%	5%
5 equiv *t*-BuHgCl dark, 35-45 °C, 44h		58%	9%

[a] Substrates with mercurial in nitrogen-purged DMSO-d_6 were irradiated with a 275 W sunlamp ca. 20 cm from the reaction flask at 35-45 °C. Substrates without mercurial were heated at 35-45 °C in the dark.

[b] O-alkyl sulfoxonium salt.

[c] S-alkyl sulfoxonium salt.

Conclusion

The reactions of propargyl derivatives with organomercurials described in this part are believed to involve free radical processes. This is based on the finding that the reactions proceed only when irradiated and the photostimulated reactions are inhibited by radical scavengers. The mechanism of substitution could be either a concerted S_H2' or a stepwise addition-elimination process. (The S_H2' acronym is usually applied to both processes.)

In the presence of I^-, the ate complex (t-$BuHgI_2^-$) is responsible for the increased yield of t-$BuCH{=}C{=}CH_2$ in the photostimulated reaction of propargyl chloride.

The reaction of propargyl tosylate with *tert*-butylmercury chloride also proceeds by a free radical chain process. Iodide ion inhibited the reaction of the tosylate, apparently by forming the propargyl iodide which could enter into the chain-terminating halogen atom transfer reaction. In DMSO propargyl tosylate was slowly converted into the sulfoxonium salts, which gave a poor yield of allene when photolyzed with *tert*-butylmercury chloride. It appears that the propargyl sulfoxonium salts are not involved in the reaction of propargyl tosylate with *tert*-butylmercury chloride under photolysis. The photostimulated reaction of propargyl tosylate with *tert*-butylmercury chloride occurs via intermediate 4, which undergoes a very rapid elimination reaction.

Experimental Section

Instrumentation and techniques

Analytical gas chromatography was performed using a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. ^{1}H NMR spectra were recorded on a 300-MHz Nicolet NT300 spectrometer with tetramethylsilane as the internal standard. GCMS were recorded on a Finnegan 4000 spectrometer; high resolution mass spectra were recorded on an AEI MS 902 mass spectrometer, and GCIR with an IBM IR-98 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected.

GLC yields were determined by using an internal standard (biphenyl or toluene) and were corrected with predetermined response factors. ^{1}H NMR spectroscopy yields were determined by integration with a known amount of an internal standard (usually biphenyl, benzene, or dichloromethane).

Solvents and chemical reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (DMSO) was distilled from calcium hydride; benzene, diethyl ether, and tetrahydrofuran were distilled from sodium metal. Other solvents were purchased and used without purification. Me_2SO-d_6 and C_6D_6 were purchased from Cambridge Isotope Laboratories and dried over 4A molecular sieves. Allyl iodide, bromide, chloride, 3-chloro-2-methyl propene and propargyl chloride were purchased from Aldrich Chemical Company. Propargyl bromide was purchased from Fluka Company. In most cases, the reagents were used without further purification.

Preparation of organomercurials

Most of the alkylmercury halides were prepared by literature procedures.[54] They were synthesized by the standard Grignard reagents and mercury salts (1: 1 equiv) in THF.

tert-Butylmercury chloride The preparation of *t*-BuHgCl in refluxing THF in the usual manner afforded a low yield (20-30%) of the product, because of the instability of the mercurial. The yield, however, can be improved to over 65% by performing the reaction at a low temperature. Thus, a solution of *tert*-butylmagnesium chloride prepared from *tert*-butyl chloride and Mg in dry THF under a nitrogen atmosphere was cooled in an ice bath while an equimolar amount of mercuric chloride in THF was added dropwise with stirring. After the addition, the mixture was then poured into 2% acetic acid in ice water containing several equivalents of sodium chloride. The white precipitate of *tert*-butylmercury chloride was filtered and dissolved in chloroform and filtered again to remove the remaining mercuric chloride. Chloroform was then removed under vacuum to give a white solid of *tert*-butylmercury chloride, which was recrystallized from hexane and dichloromethane mixture solvents mp 111-113 °C (lit.[55] sublimed point 124 °C); ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9 H).

tert-Butylmercury iodide *tert*-Butylmercury iodide was prepared by anion exchange.[56] Thus, the alkylmercury chloride was treated with a ten-fold excess of sodium iodide in methylene chloride solution for 24 hours. The reaction mixture was filtered through sintered glass and the solvent removed under reduced pressure. The *tert*-butylmercury iodide was purified by recrystallization from the mixed solvent system of methylene chloride and hexane to give light yellow crystals.
^{1}H NMR ($CDCl_3$) δ 1.43 s, 9 H).

Preparation of propargyl derivatives

Propargyl acetate[57] A solution of propargyl bromide (1 g) and sodium acetate (5 g) in DMSO (30 ml) was stirred at room temperature for several hours until the propargyl bromide disappeared (the progress of the reaction was monitored by TLC). The solution was diluted with ether, washed with water several times and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the product isolated by distillation to give 50% of propargyl acetate, bp 55 °C at 55 mmHg; ^{1}H NMR ($CDCl_3$) δ 4.68 (d, J = 2.4 Hz, 2 H, -CH_2-), 2.48 (t, J = 2.4 Hz, 1 H, HC≡C-), 2.11 (s, 3 H, CH_3-); GCMS *m /z* (relative intensity) 99 ((M+1)$^+$, 0.1), 83 0.7), 70 (4), 59 (0.7), 55 (5), 43 (100), 39 (29).

Propargyl phenyl sulfide[58] A solution of the phenyl thiol (0.042 mol) and an equimolar amount of KOH (2.36 g) in methanol (50 ml) was added dropwise with stirring to a solution of propargyl bromide (5 g, 0.042 mol) in methanol (50 ml) under nitrogen at ambient temperature. After stirring overnight, the precipitated KBr was filtered off and the solvent removed in vacuo. The crude product was dissolved in chloroform (100 ml) and washed with 0.2 N KOH (3 x 100 ml) and water (100 ml), dried over anhydrous $MgSO_4$ and solvent removed in vacuo to give a pale yellow liquid which was distilled at reduced pressure to give the sulfide, bp 55-57 °C at 0.2 mmHg.; ^{1}H NMR ($CDCl_3$) δ 7.5 (m, 5 H, C_6H_5-), 3.65 (d, J = 2.4 Hz, 2 H, -CH_2-), 2.30 (t, J = 2.4 Hz, 1 H, HC≡C-); GCMS *m /z* (relative intensity) 148 (M^+, 27), 147 (100), 115 (10), 109 (28), 77 (6), 69 (16), 65 (25), 39 (37).

Propargyl iodide[59] Propargyl iodide was prepared by reaction of propargyl bromide with sodium iodide in acetone solution. Propargyl bromide (100 mmol) was added to 100 ml of 1.5 M sodium iodide in acetone. The solution was stirred at 0 °C for 5 h until the propargyl bromide disappeared (the progress of the reaction was monitored by TLC). Using vacuum to transfer the solution to another flask, 200 ml of ether was added to the acetone solution and the resulting mixture washed with ice water several times. The ether solution was dried over anhydrous sodium sulfate. The product was purified by reduced pressure distillation at low temperature. The ^{1}H NMR spectrum of the product showed 95% of propargyl iodide and 5% of allenyl iodide; ^{1}H NMR ($CDCl_3$) δ 3.65 (d, J=2.7 Hz, 2 H), 2.42 (t, J = 2.7 Hz, 1 H); GCMS *m/z* (relative intensity) 166 (M^+, 41), 127 (12), 39 (100), 38 (20).

Propargyl tosylate[58,60] **and butyne-3-tosylate (α-methylpropargyl tosylate)**[61] Tosyl chloride (50 mmol) was dissolved in 50 ml of diethyl ether. Propargyl alcohol or butyn-3-ol was then added and the mixture cooled to between -5 and -10 °C (bath of dry ice and acetone). Freshly and finely machine-powdered KOH (200 mmol) was added with efficient stirring. The addition was initially carried out in 3 g portions with intervals of 1min. The evolution of heat was considerable and efficient cooling was necessary to maintain the temperature between -5 to 0 °C. After addition of the KOH, the mixture was then stirred for an additional 1 hour. Workup was carried out by pouring the mixture into ice water. The solid remaining in the flask was quickly hydrolyzed with ice water and subsequently added to the bulk of the solution. After vigorous shaking, the layers were separated. The organic layer and two ether extracts were dried over $MgSO_4$, after which the ether was removed in vacuo, keeping

the temperature of the heating bath below 80 °C. The product was purified by distillation or by recrystallization.

The propargyl tosylate had bp 117-118 °C at 0.1 mmHg; ^{1}H NMR (DMSO-d_6) δ 7.82 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 4.83 (d, J = 2.4 Hz, 2H, -CH_2-), 3.67 (t, J = 2.4 Hz, 1H, -C≡CH), 2.40 (s, 3H); GCMS *m / z* (relative intensity) 210 (M^+, 6), 155 (14), 139 (16), 130 (10), 118 (10), 91 (100), 77 (5), 65 (31), 39 (30).

The α-methylpropargyl tosylate had mp 44-46 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2 H), 7.35 (d, J = 8.1 Hz, 2 H), 5.20 (qd, J = 6.6, 2.1 Hz, 1 H, -CH-), 2.45 (s, 3 H, -CH_3), 2.41 (d, J = 2.1 Hz, 1 H, -C≡CH), 1.58 (d, J = 6.6 Hz, 3 H, -CH_3); GCMS *m /z* (relative intensity) 224 (M^+, 2), 172 (30), 155 (15), 144 (20), 139 (40), 129 (20), 107 20), 91 (100), 77 (10), 69 (15), 65 (40), 53 (20), 39 (20).

<u>α-Methylpropargyl chloride (3-Chloro-1-butyne)</u>[62] 1-Butyn-3-ol (70 g) and 1.5 g of pyridine were placed in a flask which was equipped with a mercury-sealed sweep-stirrer. Freshly distilled thionyl chloride (130 g) was added dropwise with moderate stirring and at the conclusion of the addition, the mixture was heated to 70 °C for 30 min. The mixture was cooled, poured on to 200 g of ice and 50 ml of ether was added. The ether layer was washed twice with water, twice with a sodium bicarbonate solution, and again with water. It was dried over anhydrous sodium sulfate and after removal of the ether the product was purified by distillation. α-Methyl propargyl chloride had bp 68-69 °C (lit.[62] bp 68.5 °C); ^{1}H NMR (DMSO-d_6) δ 4.97 (qd, J = 6.6, 2.1 Hz, 1 H, -CH-), 3.73 (d, J = 2.1 Hz, 1 H, -C≡CH), 1.68 (d, J = 6.6 Hz, 3 H, -CH_3); GCMS *m /z* (relative intensity) 90 ((M + 2) $^+$, 3), 88 (M^+, 11), 75 (12), 73 (37), 62 (6), 53 (100), 51 (38).

Propargyl phenylsulfone[58] Propargyl chloride (50 mmol) was added dropwise into a solution of sodium bezenesulfinate (60 mmol) in 50 ml of DMSO at 0 °C under nitrogen. The solution was stirred for an additional 30 min and then warmed gradually to room temperature for 3 hours. The mixture was diluted with ether and washed with water several times. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed by vacuo and the product isolated by recrystallization from the mixed solvents of hexane and methylene chloride. Propargyl phenylsulfone had mp 92-93 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (m, 2 H), 7.70 (m, 1 H), 7.59 (m, 2 H), 3.97 (d, J = 2.7 Hz, 2 H), 2.36 (t, J = 2.7 Hz, 1 H); GCMS *m/z* (relative intensity) 180 (M^+, 1.5), 141 (38), 125 (4), 116 (16), 77 (100), 51 (33).

Propargyl benzoate[63] Propargyl alcohol (50 mmol) was dissolved in dry THF (50 ml) at -70 °C, and *n*-butyllithium in hexane solution (50 mmol) was added dropwise into the solution. After the addition, the solution was stirred for 30 min. Benzoyl chloride (30 mmol), dissolved in 30 ml dry THF, was added to the solution at -70 °C. The reaction mixture was gradually warmed to room temperature and stirred overnight. Saturated aqueous ammonium chloride solution (50 ml) was added to the solution at 0 °C. The solution was extracted with ether twice. The organic layer was washed with water twice and dried over anhydrous sodium sulfate. After removal of the ether under vacuo, the product was purified by distillation to give material with bp 61-62 °C at 0.06 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.5 (m, 5 H), 4.91 (d, J = 2.4 Hz, 2 H), 2.54 (t, J = 2.4 Hz, 1 H); GCMS *m/z* (relative intensity) 160 (M^+, 10), 115 (13), 105 (100), 77 (56), 51 (29), 39 (18).

Diethyl propargyl phosphate[64] A solution of propargyl alcohol (50 mmol) in dry ether at -78 °C was treated with *n*-butyllithium hexane solution (50 mmol), followed by diethyl chlorophosphate (100 mmol) in ether-triethylamine (treatment of the chloride with triethylamine at 0 °C in ether produced a white precipitate and a clear supernatant solution which was added) at -20 °C for 20 hours. The product was purified by distillation. Diethyl propargyl phosphate had bp 66-68 °C at 0.2 mmHg; ^{1}H NMR ($CDCl_3$) δ 4.66 (dd, J = 2.4, 9.9 Hz, 2 H, $-CH_2-C{\equiv}C$), 4.15 (pentet, J = 7.2 Hz, 4 H, $-OCH_2-$), 2.57 (t, J = 2.4 Hz, 1 H, $-C{\equiv}CH$), 1.35 (t, J = 7.2 Hz, 6 H, $-CH_3$); GCMS *m/z* (relative intensity) 192 (M^+, 0.1), 136 (100), 119 (14), 99 (22), 81 (21), 57 (15), 55 (17).

Preparation of *tert*-butylallene and 4,4-dimethyl-1-pentene

***tert*-Butylallene**[65,66] *tert*-Butylmagnesium chloride (0.13 mol) in 170 ml of THF was added to a stirred mixture of 0.1 mol of propargyl tosylate in 100 ml of THF and 0.01 mol of CuBr at -30 °C. Subsequently, the temperature was allowed to rise to 20 °C and the reaction mixture poured into a saturated aqueous ammonium chloride solution, containing some NaCN. The aqueous layer later was extracted thrice with 50 ml of a high-boiling petroleum ether fraction (bp 180 °C). The combined extracts were washed ten times with 100 ml portions of water in order to remove the THF. After drying over K_2CO_3, the product was isolated by evacuating the extract at water pump vacuum and collecting the volatile products in a receiver cooled in a CO_2-acetone mixture (-80 °C). Redistillation at normal pressure afforded pure *t*-BuCH=C=CH_2, bp 73-75 °C (lit.[66] bp 73-75 °C); ^{1}H NMR (DMSO-d_6) δ 5.18 (t, J = 6.6 Hz, 1 H), 4.79 (d, J = 6.6 Hz, 2 H), 1.01 (s , 9 H); GCMS *m/z* (relative

intensity) 96 (M^+, 25), 81 (72), 79 (30), 57 (100), 53 (32), 41 (85), 39 (52), 29 (53), 27 (34).

4,4-Dimethyl-1-pentene[47] *tert*-Butyllithium (50 mmol) in pentane solution (1.7 M) was added dropwise to neat allyl chloride at -78 °C under nitrogen. After the addition was complete, the solution was stirred for an additional 1 hour. The solution was transferred to another flask by vacuum. The product was purified by distillation to give material : bp 71-72 °C; ^{1}H NMR ($CDCl_3$) 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* (relative intensity) 98 (M^+, 1.), 83 (2), 57 (100), 55 (30), 41 (48), 39 (15).

General procedure for the photostimulated reactions of propargyl and allyl derivatives with organomercurials

The substrate (0.1 M) and co-reactant (see Table 1-1 and 1-2 for equivalents) were dissolved in deoxygenated solvent under a nitrogen atmosphere in a Pyrex test tube equipped with a rubber septum. The mixture was irradiated with a 275-W sunlamp ca. 20 cm from the reaction test tube for the period time indicated in the Tables. After irradiation, a known amount of the internal standard biphenyl was dissolved in the reaction mixture. The reaction mixture was then poured into saturated aqueous sodium chloride solution and extracted with diethyl ether. The ether extract was washed twice with 20% sodium thiosulfate solution to remove any organomercury halide, dried over anhydrous sodium sulfate, and carefully concentrated under vacuum. The mixture was then analyzed by GC and GCMS.

Reaction of allyl and propargyl derivatives with *tert*-butylmercury chloride were conveniently performed in an NMR tube and monitored by ^{1}H NMR spectroscopy.

Thus, 0.1 mmol of the substrate and the co-reactant (see tables for equivalents) were dissolved in 1 ml DMSO-d_6 in an NMR tube closed with a cap and sealed with teflon tape. The ^1H NMR spectroscopy was recorded before irradiation with biphenyl or dichloromethane as the internal standard. The mixture was irradiated by a 275-W sunlamp and the progress of the reaction was monitored periodically by ^1H NMR spectroscopy. The yield of product was obtained from the integration of the appropriate peaks in the reaction product. Yields of the substitution products are summarized in Tables 1-1 and 1-2.

Identification of substitution products, in many cases, was confirmed by comparison of their ^1H NMR spectroscopy and GCMS data with those of the authentic compounds synthesized by known literature methods or by comparison of their ^1H NMR spectroscopic data with those of the compounds reported in the literature.

Reactions of propargyl acetate and benzoate with *tert*-butylmercury chloride were performed in an NMR tube and monitored by ^1H NMR spectroscopy. The reactions gave adduct organomercurials, *t*-BuCH=C(HgCl)-CH_2A', whose ^1H NMR spectra are summarized in Table 1-6. Yields of these intermediates were obtained from the integration of vinyl proton signals compared with that of an internal standard. These intermediates slowly eliminated the mercury halide and the substituent to form *tert*-butylallene.

Table 1-6. ^1H NMR spectroscopy of Photoaddition Products in DMSO-d_6

	$(CH_3)_3CCH_b=C(HgCl)C(H_c)_2A'$			
A'	CH_3 (δ)	H_b (δ)	H_c (δ)	J_{bc} (Hz)
OAc (*Z*)	1.14	5.71	4.84	2.1
OAc (*E*)	1.14	6.26	4.64	1.2
OBz (*Z*)	1.14	5.76	5.11	2.1
OBz (*E*)	1.14	6.37	4.93	1.2

General procedure for the photostimulated reactions of propargyl derivatives with *tert*-butylmercury chloride followed by sodium borohydride reduction

Propargyl acetate or benzoate (1 mmol) and *tert*-butylmercury chloride (5 mmol) was dissolved in 10 ml of DMSO in a Pyrex tube equipped with a rubber septum. After deoxygenation by a stream of nitrogen for 10 min, the mixture was photolyzed for 7 h (48 h for benzoate) under sunlamp irradiation with stirring. The mixture was added to an excess of solid sodium borohydride, 1 ml of water added and the mixture stirred for 15 min. The mixture was decanted from the mercury bead which had formed, poured into water and extracted with diethyl ether. The ether layer was washed with water twice, dried over anhydrous sodium sulfate and concentrated under vacuum.

Reduction of *t*-BuCH=C(HgCl)CH_2OAc (mixture of *E* and *Z* isomers) yielded 4,4-dimethyl-2-pentenyl acetate which had a GCMS *m/z* (relative intensity) 156 (M^+,

20), 141 (20 , 114 (5), 96 (25), 81 (40), 70 (15), 57 (20), 55 (20), 43 (100). Treatment of *t* -BuCH=C(HgCl)CH_2O_2CPh (mixture of *E* and *Z* isomers) with sodium borohydride yielded the *E* - and *Z*- isomers of 4,4-dimethyl-2-pentenyl benzoate whose *E* - and *Z*- isomers had a similar GCMS *m /z* (relative intensity) 218 (M^+, 2), 162 (5), 105 (100), 96 (10), 77 (25), 55 (20).

Formation and reaction of propargyl sulfoxonium salts with *tert*-butylmercury chloride monitored by ^{1}H NMR spectroscopy

Propargyl tosylate (0.1 mmol) was dissolved in 1 ml of DMSO-d_6 in an NMR tube at 35-45 °C. The mixture was monitored periodically by ^{1}H NMR spectroscopy, which showed one downfield and one upfield shift of the methylene hydrogen upon the formation of the mixture of sulfoxonium salts. It seems reasonable to assume that the chemical shifts of ^{1}H NMR of O-propargyl sulfoxonium salt will shift to downfield and S-propargyl sulfoxonium salt will shift to upfield. This is also consistent with that S-propargyl sulfoxonium salt is a thermodynamic product and O-propargyl sulfoxonium salt is a kinetic product.[52] The chemical shifts of ^{1}H NMR of these two intermediates are summarized in Table 1-7. The formation of the propargyl sulfoxonium salts was completed after 48 h. Photolysis of these preformed sulfoxonium salts in the presence of *t*-BuHgCl (0.5 mmol) by a sunlamp under our standard conditions gave *t*-butylallene in only about 14 % yield in 7 hours.

Propargyl tosylate (0.1 mmol) and *tert*-butylmercury chloride (0.5 mmol) were dissolved in 1 ml of DMSO-d_6 in an NMR tube in the dark at 35-45 °C. After 44 h, formation of the sulfoxonium salt was complete (by ^{1}H NMR spectroscopy). Photolysis under our standard condition for 7 h gave 15% of the *t*-butylallene.

Reaction of propargyl tosylate and *tert*-butylmercury chloride with photolysis by a 275-W sunlamp for 7 hours gave only *tert*-butylallene (70% yield). The propargyl sulfoxonium salt was not observed by ^1H NMR spectroscopy.

Table 1-7. ^1H NMR of Propargyl Tosylate and Their Sulfoxonium salts in DMSO-d_6

	A = p-$MeC_6H_4SO_3$
$HC{\equiv}CCH_2A$	δ 7.81 (d, J = 8.1 Hz, 2 H), 7.49 (d, J = 8.1 Hz, 2 H), 4.82 (d, J = 2.4 Hz, 2 H), 3.66 (t , J = 2.4 Hz, 1 H), 2.40 (s, 3 H).
$HC{\equiv}CCH_2[OS(CD_3)_2]^+A^-$	δ 7.55 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2 H), 5.03 (d, J = 2.4 Hz, 2 H), 4.09 (t, J = 2.4 Hz, 1 H), 2.28 (s, 3 H).
$HC{\equiv}CCH_2[SO(CD_3)_2]^+A^-$	δ 7.55 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2 H), 4.04 (d, J = 2.4 Hz, 2 H), 3.23 (t, J = 2.4 Hz, 1 H), 2.28 (s, 3 H).

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PART II. KINETIC CHAIN LENGTH AND RELATIVE REACTIVITIES OF ALLYL AND PROPARGYL DERIVATIVES TOWARDS *tert*-BUTYL RADICAL

Introduction

Chemical kinetics is the study of the effect of concentration on the rates of chemical reactions. Such studies have proven to be valuable in the study of reaction mechanisms and to an understanding of chemical reactivity. It will often be the case that a proposed mechanism is not unique, and other postulates may account for the data equally well. Chemical kinetics is a useful tool to narrow the range of possibilities.

Kinetic chain length is the average number of monomer (or reactant) molecules consumed for every radical which initiates a chain reaction.[1] It may also be considered to be the number of successful chain propagation steps resulting from a single original chain carrier.[2] Therefore, the magnitude of the kinetic chain length measured for a reaction under a given set of conditions can be a criterion to determine whether the reaction is a chain reaction. To calculate the kinetic chain length, the rate of chain initiation must be known. This rate is conveniently measured from the inhibition period observed with known amounts of free radical chain inhibitors. Free radical chain reactions are commonly susceptible to inhibition in which a mere trace of an inhibitor can cause a marked decrease in the initial reaction rate.

The reactions of alkylmercury halides with propargyl derivatives has been shown to be a radical process (see Part I). These reactions are believed to involve a free radical chain mechanism, since the reactions fail to occur in the dark and the reactions are

significantly retarded by the presence of 10 mol% of di-*tert*-butyl nitroxide. However, the kinetic chain lengths of these reactions are not known. In order to provide evidence to support the chain process of these reactions, it is necessary to measure the kinetic chain lengths for these reactions.

In this part, we will present the results on the determination of the kinetic chain length for the reaction of propargyl tosylate with *t*-BuHgCl in DMSO solution and study the relative reactivity of allyl derivatives and propargyl derivatives towards the *tert*-butyl radical.

Results and Discussion

Determination of kinetic chain length of the reaction between propargyl tosylate and *tert*-butylmercury chloride

An initial kinetic chain length of a radical reaction can be formulated as shown in equation 2-1. Both the initial rate and rate of initiation can be measured experimentally by following either the rate of consumption of the substrate or the rate of formation of the substitution product. The progress of the reaction of propargyl tosylate with *t*-BuHgCl can be conveniently monitored by ^{1}H NMR spectroscopy.

$$\text{Kinetic Chain Length} = \frac{\text{Initial Reaction Rate}}{\text{Rate of Initiation}} \qquad (2\text{-}1)$$

Thus, propargyl tosylate and *t*-BuHgCl in nitrogen-purged deuterated DMSO were placed in an NMR tube. The solution was irradiated with a 275 W sunlamp and was checked at different periods of time by ^1H NMR spectroscopy.

The formation of the product was determined by following the increase of the allenic proton signals of *t*-BuHC=C=CH_2 which appear at 5.18 and 4.79 ppm. The yield of the product was obtained from integration of the ^1H NMR relative spectra peaks to the internal standard (biphenyl) and the results are listed in Table 2-1. The plot of yield of the substitution product vs. time is shown in Figure 2-1(curve A).

Table 2-2 includes the results from the reaction in the presence of di-*tert*-butylnitroxide (DTBN) which was carried out under the same conditions as the reaction without DTBN. The plot of yield of the substitution product vs. time is shown in Figure 2-1 (curve B).

The initial rate of the reaction is obtained from the slope of the curve at the beginning of the reaction drawn by using a tagent meter as shown in Figure 2-1 and calculated as 6.85×10^{-2} M/min. The time for which the reaction was inhibited by 0.0288 M DTBN, is 141 min (Figure 2-1). The rate of initiation with the inhibitor (DTBN) present is obtained from the concentration of DTBN divided by the time needed to consume all of the DTBN which can be determined from Figure 2-1. The calculation, of course, assumes that DTBN captures the initiating radical in 1:1 stoichiometry.

From Figure 2-1

Initial Rate = 6.85×10^{-2} (M/min)

Rate of Initiation = $2.88 \times 10^{-2} / 141$ (M/min) = 2.04×10^{-4} (M/min)

Kinetic Chain Length = 335.7

Table 2-1. Reaction of Propargyl Tosylate with *t*-BuHgCl in DMSO-d_6[a]

$$HC{\equiv}CCH_2OTs + t\text{-BuHgCl} \xrightarrow{h\upsilon^{b}} t\text{-BuCH=C=CH}_2$$

Time (min)	% formation of *t*-BuCH=C=CH_2 without DTBN[c]
10	5
17	9
28	13
36	20
48	27
95	38
128	39
151	41
205	48
242	53
290	57
337	60
454	72

[a] The reaction of propargyl tosylate (0.1 M) and *t*-BuHgCl (0.5 M) without DTBN was carried out in 1 ml DMSO-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated with a 275 W sunlamp ca. 20 cm from the tube.

[c] Determined by ^{1}H NMR spectroscopy using biphenyl as the internal standard.

Table 2-2. Reaction of Propargyl Tosylate and *tert*-Butylmercury Chloride in the presence of DTBN in DMSO-d_6[a]

$$HC{\equiv}CCH_2OTs + t\text{-}BuHgCl + DTBN \xrightarrow{h\upsilon^{b}} t\text{-}BuCH{=}C{=}CH_2$$

Time (min)	% formation of *t*-BuCH=C=CH_2 with DTBN[c]
72	-
111	-
153	3
177	11
212	19
252	25
299	30
349	39

[a] The reaction of propargyl tosylate (0.1 M) and *t*-BuHgCl (0.5 M) with 0.0288 M DTBN was carried out in 1 ml DMSO-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated with a 275 W sunlamp ca. 20 cm from the tube.

[c] Determined by ^1H NMR spectroscopy using biphenyl as the internal standard.

Curve A : without DTBN

Curve B : with 0.0288 M DTBN

Initial rate = (6.85×10^{-1}) x 0.1 M = 6.85×10^{-2} M/min

Inhibited time = 141 min

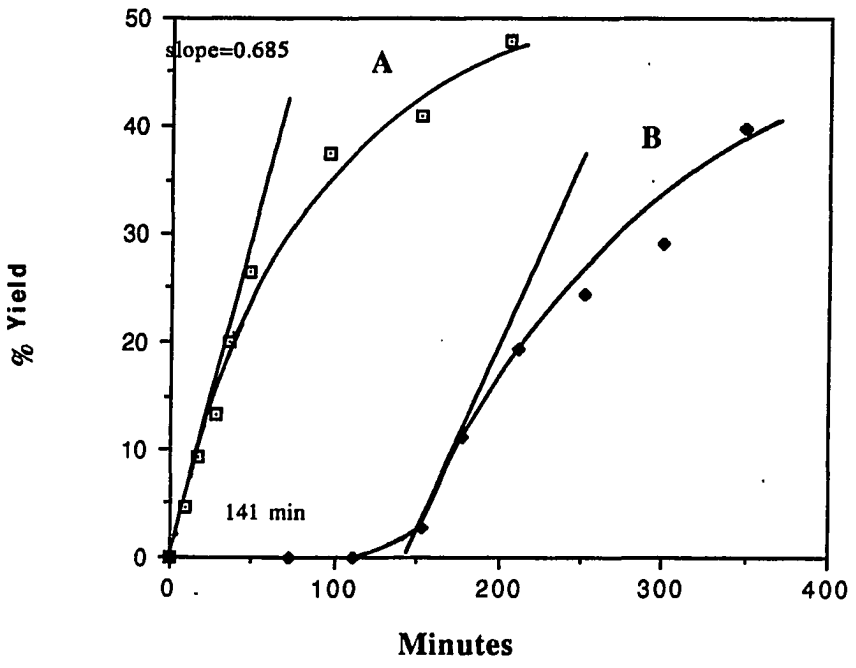

Figure 2-1. Formation of product vs. time for the reaction of propargyl tosylate and *tert*-butylmercury chloride

The reaction of propargyl tosylate with *t*-BuHgCl is definitely a radical chain process with an appreciable initial kinetic chain length of 335. The measured kinetic chain length, however, is based on the consumption of DTBN only by the *tert*-butyl radical and not by the monomeric • HgCl. In fact, the DTBN could trap both *tert*-butyl radical and • HgCl, and if •HgCl cannot initiate the chain, the initial kinetic chain length would be 335 x 2. Actually, it is believed that •HgCl can initiate the another chain by forming a *tert*-butyl radical. If the following reaction occurs, trapping or lack of trapping of the •HgCl by DTBN will have no effect on the calculation of the kinetic chain length.

$$t\text{-BuHgCl} + \bullet\text{HgCl} \longrightarrow t\text{-Bu}\bullet + \text{Hg}^{\circ} + \text{HgCl}_2$$

Relative reactivities of allyl and propargyl chloride towards *tert*-butyl radical

Competitive reactions between two substrates which individually react with *t*-BuHgCl by a chain process yield relative reactivity data concerning the product-determining steps. With long kinetic chain processes, product formation in the photoinitiation or termination steps can be ignored and product formation will be determined by the irreversible addition of *t*-Bu• to the competing substrates.

Table 2-3 summarizes the data obtained using a 5-fold excess of each of two competing substrates in DMSO at 35-40 °C under conditions where kinetic chain lengths for the individual substrates have been measured by the nitroxide-inhibition technique under typical reactive conditions as 50-70 for allyl chloride[3] and >300 for propargyl

tosylate (all measurements with a 2-5 fold excess of *t*-BuHgCl; longer kinetic chain lengths are probable when the radicaphile is used in excess).

Allyl chloride was 10 times as reactive as propargyl chloride and 3.6 times more reactive than propargyl tosylate in direct competition experiment. The kinetic chain length of the reaction of propargyl chloride with *t*-BuHgCl has not been measured, but is presumably about 0.1 that of allyl chloride since both reactions involve the same chain-carrying chlorine atoms and *tert*-butyl radicals. The relative reactivities of propargyl and allyl chlorides were not affected by the presence of iodide ion, which is apparently not involved in the step (radical addition) that determines which product will be formed. In the presence of NaI, slow, thermally initiated free radical reactions occurred which also gave a relative reactivity of allyl chloride to propargyl chloride of ~ 10.

Table 2-3. Relative reactivities toward *tert*-butyl radical at 35-40 °C in DMSO-d_6

substrate A(0.5M)	substrate B(0.5M)	conditions[a]	k_a/k_b[b]	rel react. of A
$HC{\equiv}CCH_2Cl$	$CH_2{=}CHCH_2Cl$	6 h	0.10	0.1
$HC{\equiv}CCH_2OTs$	$CH_2{=}CHCH_2Cl$	5 h	0.28	0.28
$CH_2{=}C(Me)CH_2Cl$	$CH_2{=}CHCH_2Cl$	5 h	0.8	0.8

[a] Substrates and 0.1 M *t*-BuHgCl in DMSO-d_6 with photolysis by a 275 W sunlamp ca. 20 cm from the reaction vessel.

[b] By ^1H NMR spectroscopy of the substitution products.

Table 2-4 examines the relative reactivities of $HC{\equiv}CCH_2Cl$ (**P**), $CH_2{=}CHCH_2Cl$ (**A**) and $CH_2{=}C(Me)CH_2Cl$ (**MA**) towards a variety of *tert*-butylating reagents. The experiments involved the competition of 1 equiv of **A** and 1 equiv **P** or **MA** with 0.1-0.2 equiv of organometallic reagent, and the relative reactivities are based on the yields of *t*-$BuCH_2CH{=}CH_2$ and *t*-$BuCH{=}C{=}CH_2$ or *t*-$BuCH_2C(Me){=}CH_2$ measured by GLC or ^1H NMR spectroscopy (in DMSO-d_6).

The relative reactivities observed with *t*-BuHgCl under fluorescent irradiation were not effected by the presence of of I^- in DMSO or by a change in solvent from DMSO to Et_2O. At 35 °C the relative reactivities towards *t*-Bu• generated from *t*-BuHgCl were **P: A: MA** = 0.096 ± 0.007 : 1.00 : 0.84 ± 0.02 while with (*t*-$Bu)_2CuLi$ in Et_2O at -78 °C relative reactivities were 0.097 ± 0.005 : 1.00 : 0.64 ± 0.04. With (*t*-$Bu)_2Cu(CN)Li_2$ the relative reactivity of **A** and **MA** decreased from 1.00 : 0.79 ± 0.04 at 0 °C to 1.00 : 0.53 ± 0.01 at -78 °C while with (*t*-$Bu)_3ZnLi$ / TMEDA at 0 °C a relative reactivity of 1.00 : 0.69 ± 0.01 was observed.

For competition between allyl and methallyl chloride, the data can be interpreted as indicating *t*-Bu• attack for all the reagents with an energy of activation favoring attack upon allyl chloride. However, the possibility exists that the relative reactivities measured for this pair of substrates is insensitive to the nature (radical, anionic) of the *tert*-butylating species. On the other hand, competitive reactions of these reagents with propargyl and allyl chloride gave different relative reactivities. The relative reactivities observed with (*t*-$Bu)_2CuLi$ of **P : A** = 0.097 ± 0.005 at -78 °C and 0.086 ± 0.005 at 0 °C are consistent with *t*-Bu• attack. (With *t*-BuLi a low yield of alkylation product was observed in which *t*-$BuCH_2CH{=}CH_2$ greatly predominated.) However, with (*t*-$Bu)_2Cu(CN)Li_2$ at 0 or -78 °C, propargyl chloride was 1.3-1.7 as reactive as allyl chloride while with (*t*-$Bu)_3ZnLi$ / TMEDA, the propargyl chloride was more than 5

Table 2-4. Relative reactivity in *tert*-butylation reactions

conditions	relative reactivity[a] (P)[b]	(A)[c]	(MA)[d]
t-BuHgCl / DMSO-d_6 / *hv* / 35 °C	0.096 ± 0.007	1.00	0.84 ± 0.02
t-BuHgCl / Et_2O / *hv* / 35 °C	0.09	1.00	0.84
$(t\text{-Bu})_2CuLi$ / Et_2O / *hv* / -78 °C	0.097 ± 0.005[e]	1.00	0.64 ± 0.04
$(t\text{-Bu})_2Cu(CN)Li_2$ / Et_2O / -78 °C	1.2-1.7	1.00	0.53 ± 0.10
$(t\text{-Bu})_2Cu(CN)Li_2$ / Et_2O / 0 °C	1.2-1.3	1.00	0.79 ± 0.04
$(t\text{-Bu})_3ZnLi$ / TMEDA / Et_2O / 0 °C	5.0-7.6	1.00	0.69 ± 0.01
t-BuCuPBu_3 / Et_2O / 0, -30, -78 °C	1.8-1.9	1.00	
$(t\text{-Bu})_2Cu(SMe_2)Li$ / Et_2O / 0, -78 °C	1.0	1.00	

[a] Standard deviation are given where 5 or more experiments were performed.

[b] P = $HC{\equiv}CCH_2Cl$.

[c] A = $CH_2{=}CHCH_2Cl$.

[d] MA = $CH_2{=}C(Me)CH_2Cl$.

[e] 0.086 ± 0.005 for $(t\text{-Bu})_2CuLi$ prepared at -78 °C and reacted at 0 °C.

times as reactive. Furthermore, with $(t\text{-Bu})_2Cu(CN)Li_2$ and $(t\text{-Bu})_3ZnLi$ / TMEDA, the reproducibility was poor in contrast to $(t\text{-Bu})_2CuLi$. This perhaps reflects competing reactions. However, it seems certain that $(t\text{-Bu})_2Cu(CN)Li_2$ and $(t\text{-Bu})_3ZnLi$ / TMEDA must be able to react with propargyl and possibly allyl chloride by a mechanism that does not involve exclusively t-Bu• addition to the carbon-carbon multiple bond. With the less stable $(t\text{-Bu})_2CuLi$, a radical process, e.g., Scheme 2-1, seems to dominate for both the allyl and propargyl substrates.

Scheme 2-1

$$t\text{-Bu}\bullet + CH_2{=}CHCH_2Cl \longrightarrow t\text{-Bu}\dot{C}H_2CHCH_2Cl$$

$$t\text{-Bu}CH_2\dot{C}HCH_2Cl \longrightarrow t\text{-Bu}CH_2CH{=}CH_2 + Cl\bullet$$

$$Cl\bullet + (t\text{-Bu})_2CuLi \longrightarrow LiCl + (t\text{-Bu})_2Cu\bullet$$

$$(t\text{-Bu})_2Cu\bullet \longrightarrow t\text{-Bu}\bullet + t\text{-BuCu}$$

Conclusion

The initial kinetic chain length of the reaction of propargyl tosylate with t-BuHgCl was determined. The measured initial kinetic chain length is 335 (or 335 x 2). This result indicates that the reaction of propargyl tosylate with t-BuHgCl is definitely a

radical chain process and that most of the substitution product must be formed in the propagation step.

The relative reactivity of allyl and propargyl chlorides with *t*-BuHgCl is independent of the presence of I^- and is not effected by a change in solvent from DMSO to diethyl ether. It seems certain that for $(t\text{-Bu})_2CuLi$, a radical substitution process is dominant for both the allyl and propargyl chlorides. However, $(t\text{-Bu})_3ZnLi$ and $(t\text{-Bu})_2Cu(CN)Li_2$ must be able to react, at least partially, with propargyl and possibly allyl chloride by a mechanism that does not involve *t*-Bu• attack at the carbon-carbon multiple bond.

Experimental Section

General considerations

^1H NMR spectra were recorded on a Nicolet Magnetic Corp. NMC-1280 spectrometer (300 MHz) in DMSO-d_6. Product yields were determined by ^1H NMR spectroscopy integration with a known amount of biphenyl or by gas chromatographic analysis performed on a 3700 Varian Gas Chromatograph with a packed Chromosorb W (80-100 mesh) column coated with 7% OV-3 and a thermal conductivity detector. Product yields were determined by addition of a known amount of biphenyl or naphthalene as an internal standard.

t-BuHgCl and propargyl tosylate were prepared as previous described (see Part I). Allyl chloride, methallyl chloride, and propargyl chloride were purchased from Aldrich Chemical Company and used without further purification. Solvents were purchased and dried as mentioned in Part I.

Determination of initial kinetic chain length of the reaction of propargyl tosylate with *tert*-butylmercury chloride

Propargyl tosylate (0.5 mmol), *t*-BuHgCl (2.5 mmol) and biphenyl (0.5 mmol) were dissolved in 5 ml of nitrogen-purged deuterated DMSO. The solution was divided into ten NMR tubes (0.5 ml in each tube) which equipped with rubber septa. After a 300 MHz ^{1}H NMR spectrum was obtained, the NMR tubes were irradiated at 35-40 °C with a 275 W sunlamp placed about 20 cm from the reaction tube. The yield of substitution product (*t*-BuCH=C=CH_2) was obtained from the integration of the ^{1}H NMR allenic protons after various reaction times (Table 2-1).

The reaction of propargyl tosylate with *t*-BuHgCl in the presence of DTBN was carried out under the same conditions. The concentration of DTBN was 2.88 x 10^{-2} M. After a 300 MHz ^{1}H NMR spectrum was obtained, the NMR tubes were irradiated at 35-40 °C with a 275 W sunlamp placed about 20 cm from the reaction tubes. The yields of the substitution product at different periods of time are presented in Table 2-2.

General procedure for the competitive reactions of propargyl and allyl derivatives with di-*tert*-butylcuprate

A solution of copper(I) iodide (1.0 mmol), which had been purified by a literature procedure,[4] in dry ether (9 ml) under nitrogen was cooled to -78 °C at which temperature 1.7 M *tert*-butyllithium in pentane solution (2 mmol) was added dropwise over a period of 1 min.. The solution was stirred at -78 °C for 30 min followed by the addition of a mixture of propargyl chloride (5 mmol) and allyl chloride (5 mmol) to the solution at -78 °C or 0 °C. The solution was stirred for another 30 min at -78 °C or 0 °C. Saturated aqueous ammonium chloride solution (2 ml) was added at 0 °C and the

mixture stirred at 0 °C for 10 min before dilution with ice water; 1 mmol of biphenyl was added as an internal standard; the organic products were extracted by ether and the ether extract washed with ice water several times and dried over anhydrous sodium sulfate. The solution was concentrated by distillation and the products analyzed by GLC.

General procedure for the competitive reactions of propargyl and allyl derivatives with lithium tri-*tert*-butylzincate

A solution of $ZnCl_2$ / TMEDA complex (1 mmol), which was prepared by the literature method,[5] in dry ether (9 ml) under nitrogen was cooled to -78 °C at which temperature 1.7 M *tert*-butyllithium in pentane solution (3 mmol) was added dropwise over a period of 1 min. The solution was stirred at 0 °C for 60 min followed by the addition of a mixture of propargyl chloride (5 mmol) and allyl chloride (5 mmol) to the solution at -78 °C or 0 °C. The solution was stirred for another 60 min at -78 °C or 0 °C. Saturated aqueous ammonium chloride solution (3 ml) was added at 0 °C and the mixture stirred at 0 °C for 10 min before dilution with ice water; 1 mmol of biphenyl was added as an internal standard; the organic products were extracted by ether and the ether extract washed with ice water several times and dried over anhydrous sodium sulfate. The solution was concentrated by distillation and the products analyzed by GLC.

General procedure for the competitive reactions of propargyl and allyl derivatives with lithium di-*tert*-butylcyano cuprate

A mixture of CuCN (1.0 mmol) and dry ether (9 ml) under nitrogen was cooled to -78 °C at which temperature 1.7 M *tert*-butyllithium in pentane solution (2 mmol) was added dropwise with gently stirring. The mixture was warmed slowly to between -30 °C and 0 °C until complete dissolution of the CuCN had occurred.[6] The solution was recooled to -78 °C followed by the addition of a mixture of propargyl chloride (5 mmol) and allyl chloride (5 mmol). The solution was stirred for another 30 min at -78 °C or 0 °C. Saturated aqueous ammonium chloride solution (2 ml) was added at 0 °C and the mixture stirred at 0 °C for 10 min before dilution with ice water; 1 mmol of biphenyl was added as an internal standard; the organic products were extracted by ether and the ether extract washed with ice water several times and dried over anhydrous sodium sulfate. The solution was concentrated by distillation and the products analyzed by GLC.

General procedure for the competitive reactions of propargyl and allyl derivatives with $(t\text{-Bu})_2Cu(Me_2S)Li$[7]

A solution of the dimethyl sulfide complex of cuprous bromide (1 mmol), dry ether (5 ml) and dimethyl sulfide (5 ml) under nitrogen was cooled to -78 °C, at which temperature 1.7 M *tert*-butyllithium in pentane solution (2 mmol) was added dropwise over a period of 1 min. The solution was stirred at -78 °C for 30 min followed by the addition of a mixture of propargyl chloride (5 mmol) and allyl chloride (5 mmol) to the solution at -78 °C or 0 °C. The solution was stirred for another 30 min at -78 °C or 0 °C. Saturated aqueous ammonium chloride solution (2 ml) was added at 0 °C and the mixture stirred at 0 °C for 10 min before dilution with ice water; 1 mmol of biphenyl

was added as an internal standard; the organic products were extracted by ether and the ether extract washed with ice water several times and dried over anhydrous sodium sulfate. The solution was concentrated by distillation and the products analyzed by GLC.

General procedure for the competitive reactions of propargyl and allyl derivatives with *t*-BuCuPBu$_3$

A solution of CuI (1.0 mmol) and PBu_3 (1.0 mmol) and dry ether (9 ml) was stirred at room temperature under nitrogen until the solution became clear and then cooled to -78 °C. 1.7 M *tert*-Butyllithium in pentane solution (2 mmol) was added dropwise over 3 min. The solution was stirred at -78 °C for 30 min followed by the addition of a mixture of propargyl chloride (5 mmol) and allyl chloride (5 mmol) at -78 °C. The solution was stirred for another 30 min at -78 °C or -30 °C or 0 °C. Saturated aqueous ammonium chloride solution (2 ml) was added at 0 °C and the mixture stirred at 0 °C for 10 min before dilution with ice water; 1 mmol of biphenyl was added as an internal standard; the organic products were extracted by ether and the ether extract washed with ice water several times and dried over anhydrous sodium sulfate. The solution was concentrated by distillation and the products analyzed by GLC.

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PART III. SUBSTITUENT AND LEAVING GROUP EFFECTS IN THE REACTIONS OF ALLYL AND PROPARGYL DERIVATIVES WITH *tert*-BUTYLMERCURY CHLORIDE

Introduction

Giese[1] has reported that the rate of addition of alkyl radicals to alkenes is controlled mainly by the polar effects of the substitutents. The substituent effects can be described by Frontier Molecular Orbital theory.[2] To a first approximation, the FMO theory states the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the alkene are decisive in determining the reaction rate. The smaller the energy gap between these frontier orbitals, the larger is the stabilizing effect when the reactants approach one another. The frontier orbital of a free radical is the SOMO (singly occupied molecular orbital). Thus, the interaction between the SOMO of the free radical and the LUMO and HOMO of the alkene should play a decisive role in the interpretation and prediction of polar effects.

Electron withdrawing substituents in the alkene, which lower the LUMO energy, increase the addition rate by reducing the SOMO-LUMO energy gap. Thus, cyclohexyl radicals react 8500 times faster with acrolein than with 1-hexene.[3]

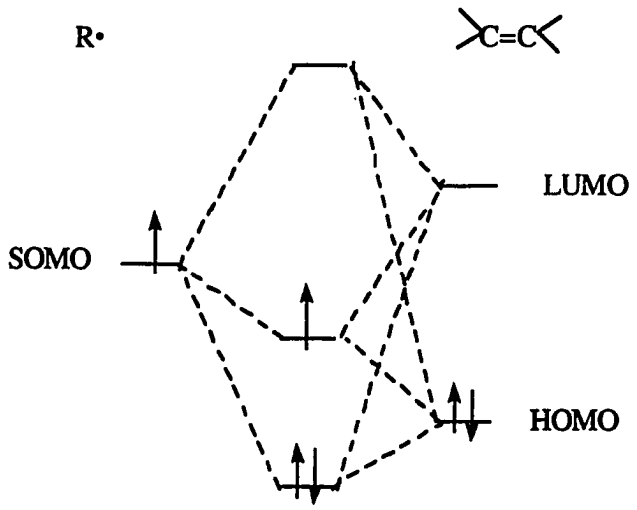


Figure 3-1. Interaction between the SOMO of a free radical and the HOMO and LUMO of an alkene

The LUMO of alkynes lies higher, and the HOMO lower, than for an alkene.[4] The interaction between the SOMO of the free radical and the frontier orbitals of the π-system is smaller for alkynes than for alkenes. Hence, *tert*-butyl radical reacts faster with alkenes than with alkynes.

Recently, Tedder and Walton[5] and Giese[6] have reviewed the rates and orientations of the free radical addition to olefins. In general, the rates and orientations are heavily influenced by the nature and the positions of substituents. Very important rules and conclusions were established which in the formulation of Giese[6] are as follows : (1) Substituents at the not attacked carbon atom of the olefin (β-substituents) exert essentially only polar effects on the rate of addition. (2) Substituents at the attacked carbon atom (α-substituents) exert both polar and steric effects on the reaction rate. (3)

Radical substituents induce polar and steric effects. (4) The addition of alkyl radicals to alkenes is characterized by an early transition state and the polar substituent effect can be described in terms of frontier molecular orbital theory. (5) The regioselectivity is determined by the steric substituent effect.

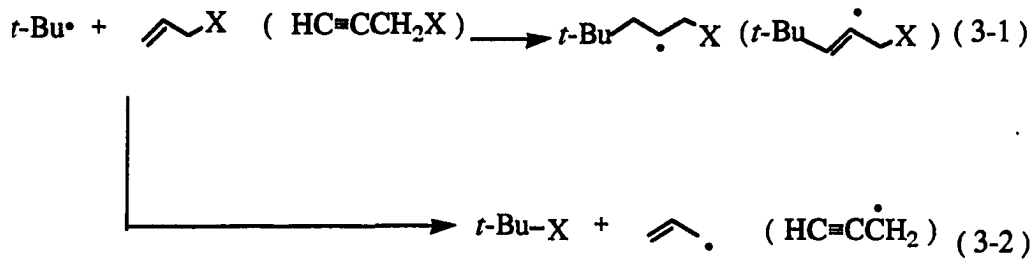
In this part, we will discuss the substituent and leaving group effects in the free radical reactions of allyl and propargyl derivatives.

Results and Discussion

The substituent and leaving group effects in the reactions of allyl derivatives

From Table 1-1, the reaction of propargyl chloride with *t*-BuHgCl in the presence of I^- gave a good yield of *tert*-butylallene. The yields of *tert*-butylallene decreased significantly when the leaving group was changed from chloride to bromide or iodide. α-Methylpropargyl chloride under the same reaction condition did not give the substituted allene. Propargyl tosylate gave a 72% yield of *tert*-butylallene when photolyzed with *t*-BuHgCl. While α-methylpropargyl tosylate gave a modest yield of *t*-BuCH=C=CHMe (34 %). In contrast to propargyl halides, the reaction of allyl halides with *t*-BuHgCl , gave good yields of *t*-$BuCH_2CH=CH_2$ with a variety of different leaving group (Table 1-2). Even methallyl chloride gave a high yield of 2,4,4-trimethyl-1-pentene.

tert-Butyl radical may react with allyl and propargyl halides by addition to multiple bonds (Eq. 3-1), or by halide-abstraction (Eq. 3-2).



The reaction of *tert*-butyl radical with allyl and propargyl derivatives is controlled by the following factors : (1) the energy gap between the SOMO of *tert*-butyl radical and the LUMO of substrates and (2) the bond dissociation energy of C-X. Thus, high yields of 4,4-dimethyl-1-pentene and no 1,5-hexadiene was observed for the reaction of *t*-BuHgCl with allyl halides. The halogen-abstraction reaction is a minor process in the allylic system and *tert*-butyl radical addition to the double bond is the major process in the photostimulated reaction of *t*-BuHgCl with allyl halides. The reason might be that the energy difference between the SOMO of the *tert*-butyl radical and the LUMO of the halides is so small that addition of a radical to the double bond is a major pathway. The SOMO-LUMO energy gap is small for the reaction of the *tert*-butyl radical with allyl halides so that variation of substituents on the allyl halides exerts a large effect on the rate. Thus, under comparable conditions, the yields of substitution product decreased from 80% for allyl chloride to 63% for 3-chloro-2-methylpropene and the yields of substitution product for $H_2C{=}CHCH_2X$ decreased according to following series: X = Cl ≈ Br > I > SPh > $SiMe_2Cl$ > $SiMe_3$.

Russell and co-workers[7] have reported that substituted phenylacetylenes (PhC≡CQ with Q = $PhSO_2$, I, SPh, Bu_3Sn) undergo free radical chain substitution reactions with

cyclohexylmercury chloride. The relative reactivities of PhC≡CQ toward *c*-C_6H_{11}• are Q = $PhSO_2$ (60) > I (19) > SPh (4) > Bu_3Sn (1). The correlation between the relative reactivities of PhC≡CQ toward *c*-C_6H_{11}• and the Hammett σ_m constants of Q gives a straight line with a good correlation coefficient of 0.976 and a ρ value of 3.05 (Fig. 3-2). This indicates that the inductive effect of Q plays an important role in free radical addition to phenylacetylene derivatives.

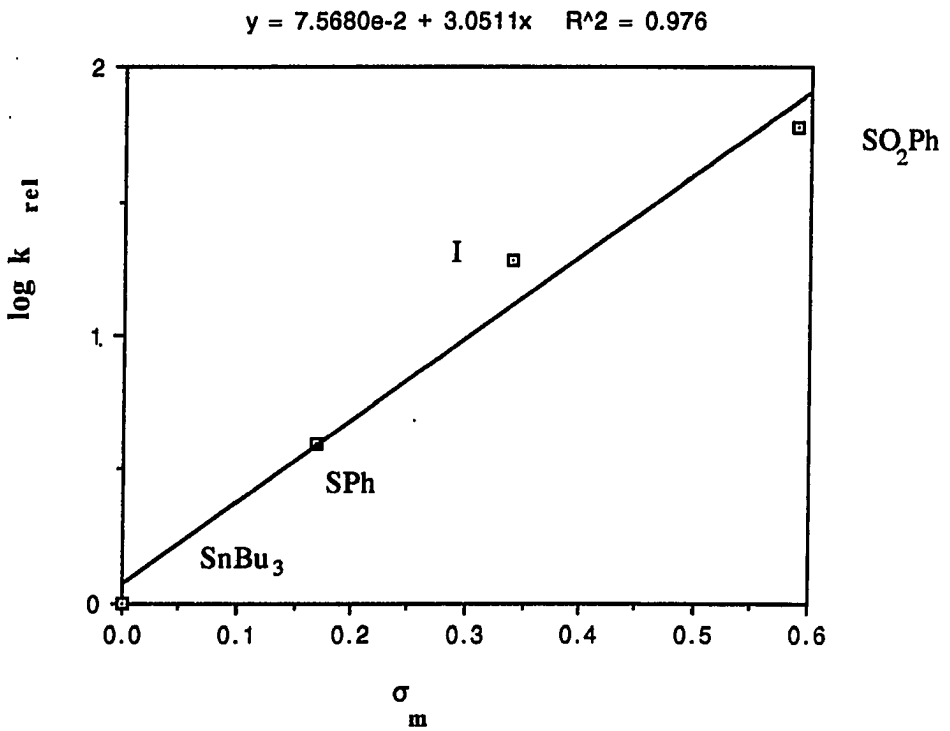
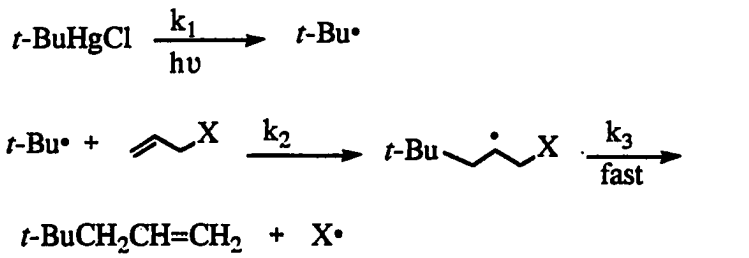


Figure 3-2. The correlation between the relative reactivities of PhC≡CQ toward cyclohexyl radical and σ_m of Q

The reaction mechanism of *t*-BuHgCl with allyl derivatives was proposed by Russell and Ngoviwatchai[8] as shown in Scheme 1-8 (page 19). The initiation rate constant for photodissociation of *t*-BuHgCl is k_1 and the rate constant of *tert*-butyl radical addition to the double bond is k_2. If the adduct radical (*t*-$BuCH_2C^{\bullet}HCH_2X$) only reacts by β-elimination, under steady state conditions, the rate of formation of *t*-$BuCH_2CH{=}CH_2$ and the rate of consumption of $CH_2{=}CHCH_2X$ will be equal; this will obviously be the case where $k_3 >> k_2$.



$$\text{Rate} = \frac{d[\,t\text{-}BuCH_2CH{=}CH_2]}{dt} = \frac{-d[\,CH_2{=}CHCH_2X\,]}{dt}$$

$$= k_2\,[\,t\text{-}Bu^{\bullet}\,]\,[\,CH_2{=}CHCH_2X\,]$$

Experimentally, reactions under standard conditions with excess *t*-BuHgCl gave an overall rate which was first order in $CH_2{=}CHCH_2X$. This is consistent with a process in which the steady state concentration of *t*-Bu• is independent of the concentration of $CH_2{=}CHCH_2X$. The pseudounimolecular rate constants calculated from the expression

$$\frac{d[\,t\text{-}BuCH_2CH{=}CH_2]}{dt} = k_{obs}\,[\,CH_2{=}CHCH_2X\,]$$

are given in Table 3-1. The plot of the logarithm of these rate constants against the Hammett σ_m constant of leaving group is shown in Fig. 3-3. The plot gives a very good correlation coefficient of 0.994 with a ρ value of 3.24. The positive sign of ρ value indicates that the *tert*-butyl radical is nucleophilic. The ρ value for the allyl system is greater than that observed for the phenylacetylene system. This suggests that the allyl system is more sensitive to the substituent inductive effect than the phenylacetylene system, even though the substituent is at the β position to the double bond in the allyl system and at the α position to the triple bond in the phenylacetylene system. This is consistent with a smaller SOMO-LUMO energy gap in the allyl system so that the substituent exerts a larger effect.

The rate constants, k_{obs}, were experimentally measured with good correlation coefficients of 0.92~ 0.99 (Table 3-1). This indicates that the kinetic assumptions made previously are reasonable. The results imply that the leaving group kinetically only exerts its inductive effect in the reactions of the allyl derivatives with *t*-Bu•. This might be the reason that the reaction of allyltrimethylsilane (σ_m for $SiMe_3$ is -0.04) with *t*-BuHgCl in DMSO under sunlamp irradiation for 7 h did not give any of the substitution product. However, although it appears that the steady state concentration of *t*-Bu• is constant throughout the reaction of an individual allyl substrate, it is difficult to prove that the same steady state concentration of *t*-Bu• was actually involved with different allylic substrates although the observed Hammett correlation suggests that this is indeed the case. If all of the leaving group radicals (X•) rapidly react with *t*-BuHgCl to generate *t*-Bu• (i.e., X• is not involved in the termination process), the steady state concentration of *t*-Bu• should depend only upon the rate of photoinitiation (held constant) and the termination reaction (possibly the combination of *t*-Bu• and •HgCl).

Table 3-1. The rate constants of the reactions of allyl and propargyl derivatives with 5 equiv of *t*-BuHgCl in DMSO

Substrate[a]	k_{obs},min^{-1} [b]	γ[c]
H_2C=$CHCH_2Cl$	1.30 x 10^{-4}	0.993
H_2C=$CHCH_2Br$	1.24 x 10^{-4}	0.996
H_2C=$CHCH_2SPh$	2.50 x 10^{-5}	0.915
H_2C=$CHCH_2SiMe_2Cl$	1.44 x 10^{-5}	0.999
H_2C=$CHCH_2SiMe_3$	-[d]	
HC≡CCH_2Cl[e]	6.17 x 10^{-5}	0.996
HC≡CCH_2OTs	3.84 x 10^{-5}	0.986

[a] The mixture in a 5 mm NMR tube was irradiated with a 275 W sunlamp ca. 20 cm from the tube; the initial concentration of the substrate was 0.1 M.

[b] k_{obs} was determined by the ^{1}H NMR spectroscopy.

[c] γ = correlation coefficient.

[d] No substituted products were observed after 7 hours under the sunlamp.

[e] The reaction was carried out in the presence of 5 equiv of NaI.

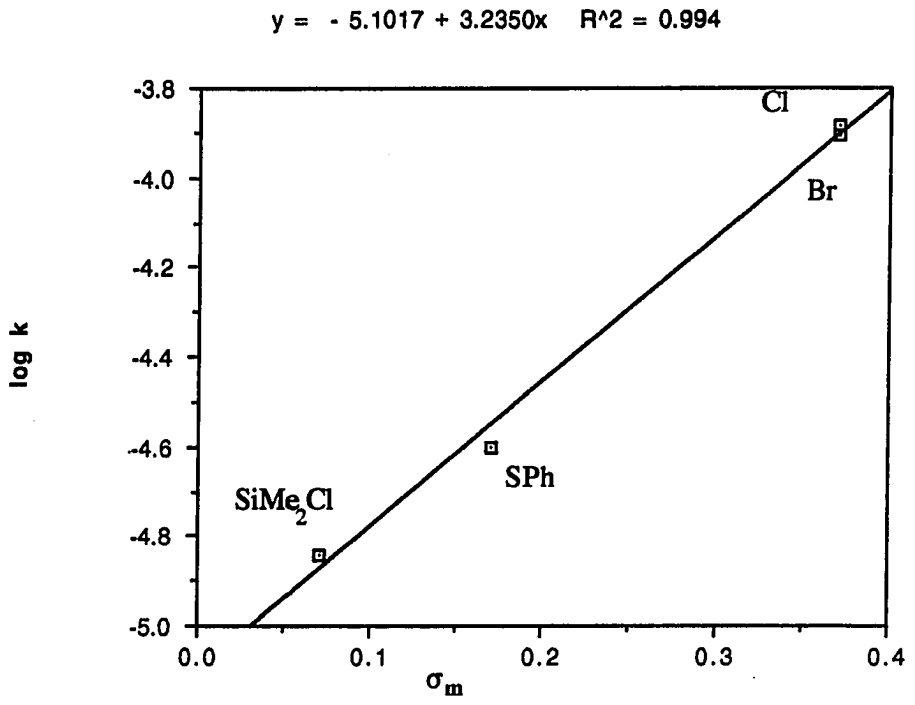


Figure 3-3. Correlation between the rate constants of the reaction of allyl derivatives with *t*-BuHgCl and the Hammett σ_m constant of the leaving groups

The substituent and leaving group effects in the reactions of propargyl derivatives

We tried to measure the rate constant, k_{obs}, for the reaction of propargyl derivatives with *t*-BuHgCl in the presence and absence of NaI. Unfortunately, we did not succeed except for the chloride and tosylate. The observed unimolecular rate constants were approximately equal for the reactions of propargyl chloride with *t*-BuHgCl (in the presence of iodide ion) and for propargyl tosylate in the absence of iodide ion. The correlation between the yields of *tert*-butylallene from Table 1-1 against σ_m of leaving group is poor (Fig. 3-4). This illustrates that the mechanisms of the reaction of *t*-BuHgCl with propargyl derivatives are quite dependent upon the leaving group. Radical addition to the triple bond (Eq. 3-1) is the dominant process in the reaction of *t*-BuHgCl with propargyl chloride in the presence of iodide ion, while halogen atom-abstraction (Eq. 3-2) apparently becomes more competitive with propargyl bromide or iodide. Giese and Lachhein[9] have reported that the alkynes react 3.0-5.2 times slower with nucleophilic alkyl radicals than the corresponding substituted alkenes. The lower rate of addition of alkyl radicals to alkynes can be accounted for by the fact that the LUMO of an alkyne is energetically higher than the LUMO of an alkene. Thus, k(allyl chloride) / k (propargyl chloride) ≅ 10 and k_{obs} for propargyl chloride is much greater than that for bromide or iodide; the SOMO-LUMO energy gap for the propargyl system reaction with *t*-Bu• is larger than that for the allyl system and that for bromide or iodide is larger than that for chloride in the propargyl system. The bond dissociation energies for C-Br and C-I, which are much less than that for C-Cl (Table 3-2), favors the halogen atom-abstraction for bromine or iodine. In contrast to the allyl halides, the halogen atom-abstraction reaction for propargyl iodide and bromide becomes a relatively facile process.

These leads to the production of the propargyl radical which may undergo chain termination with a resulting decrease in the steady state concentration of *t*-Bu•.

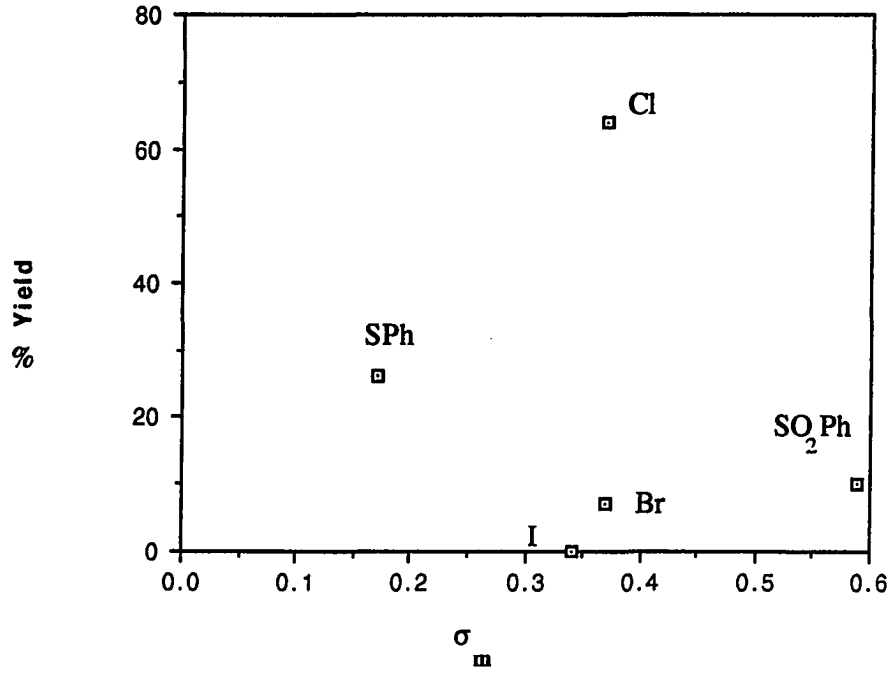


Figure 3-4. Correlation between the yields of substituted product in the reaction of propargyl derivatives with *t*-BuHgCl in the presence of NaI and the Hammett σ_m constants of the the leaving groups

Table 3-2. The bond dissociation energy of C-X [a]

Bond	Energy (kcal $mole^{-1}$)
$Cl\text{-}CH_3$	83.5
$Br\text{-}CH_3$	70
$I\text{-}CH_3$	56
C-O	84
O-S	125
C-S	167

[a] From T. H. Lowry; K. S. Richardson *Mechanism and Theory in Organic Chemistry* ; 2nd ed., Harper & Row: New York, 1981; p 147.

The abstraction of the leaving group by the *tert*-butyl radical is an unimportant process for propargyl chloride and tosylate because the inductive effect of chloride and OTs reduces the SOMO-LUMO energy gap for the addition of *t*-Bu• while at the same time the high bond dissociation energy for C-O and C-Cl (Table 3-2) disfavors S_H2 substitution at the leaving group. The reaction of α-methylpropargyl chloride with *t*-BuHgCl did not give the substituted product and the starting material could be partially recovered. Halogen atom abstraction appears to be a major pathway because the methyl inductive effect increases the SOMO-LUMO energy gap while at the same time chlorine atom abstraction leads to a radical which is both 2° and propargylic. Thus, the halogen atom-abstraction reaction is favored over radical addition to the triple bond. The reaction of α-methylpropargyl tosylate with *t*-BuHgCl gave a modest yield (38%) of the expected product, 1-*tert*-butyl-3-methylallene. In this case, radical attack at the tosylate is unlikely and addition to the triple bond can be observed. Propargyl phenyl sulfone was predicted to give a high yield of the substituted allene, because of the large σ_m value for the sulfone group. However, only 26% of the substituted allene was obtained. However, propargyl phenyl sulfone is very easily isomerized to allenyl phenyl sulfone which may explain the low yield observed for *t*-BuCH=C=CH_2.

The mechanisms of the reaction of propargyl derivatives with *t*-BuHgCl in the presence or absence of I^- are diverse. The reactions of propargyl chloride and tosylate give good yields of *t*-BuCH=C=CH_2 in processes which are kinetically 1st order with respect to the propargyl derivative and follow the S_H2' mechanism discussed in Part I. However, the reactions of propargyl iodide and bromide gave low yields of *t*-BuCH=C=CH_2, because the dominant reaction switches from radical addition to the triple bond to halogen atom-abstraction.

Russell and co-workers[10] have reported that the effect of iodide ion may involve electron transfer from I^- or *t*-$BuHgI_2^-$ to the electron accepting adduct radical or eliminated radical shown in Reactions 3-3 and 3-4 (A• = electron accepting radical).

$$A\bullet + I^- \longrightarrow A^- + I\bullet \xrightarrow{t\text{-BuHgI}} HgI_2 + t\text{-Bu}\bullet \quad (3\text{-}3)$$

$$A\bullet + t\text{-BuHgI}_2^- \longrightarrow A^- + HgI_2 + t\text{-Bu}\bullet \quad (3\text{-}4)$$

A decision in favor of Reaction 3-4 can be made in the free radical reaction between *i*-PrHgI and $BrCCl_3$, a process which also displays dramatic acceleration by iodide ion. The reaction involves electron transfer from *i*-$PrHgI_2^-$ to the trichloromethyl radical in a long kinetic chain process (Eqs. 1-12 and 1-13) (page 27).

The relative reactivities of allyl and propargyl chloride with *t*-BuHgCl under fluorescent irradiation were not effected by the presence of I^- in DMSO, i.e., k_{allyl} / $k_{propargyl} \cong 10$. This means that the mechanism of the reaction with I^- is similar to that without I^- as far as the radical addition step is concerned. The reactions in the presence and absence of iodide were 1st order in propargyl chloride. This suggests that the intermediate adduct radical is not involved in chain termination and is readily converted to the allene in the presence or absence of I^-. The acceleration by I^- must be the result of a higher steady state concentration of *t*-Bu• resulting from a faster rate of initiation and/or a more efficient recycling of the eliminated chlorine atom to regenerate *t*-Bu•.

The pseudounimolecular rate constant measured from product formation for the reaction of propargyl tosylate had a good correlation coefficient. This is further evidence that intermediate 4, *t*-$BuCH=C(HgCl)CH_2OTs$, undergoes a very rapid elimination of HgCl and OTs. The relative reactivity, k_P / k_A, of propargyl tosylate and allyl chloride

towards *t*-Bu• was measured directly in a competitive reaction as 0.28.[8] The ratio of k_{obs} for propargyl tosylate to k_{obs} for allyl chloride is 0.29, suggesting that in the absence of I^- that the steady state *t*-Bu• concentration was the same for both of these photostimulated processes. In the presence of I^-, the reaction of propargyl chloride was greatly accelerated while the tosylate was drastically retarded (because of propargyl iodide formation).

Conclusion

Substituent and leaving group effects play a dominant role in the free radical reaction of propargyl and allyl derivatives with *t*-BuHgCl. Reactions of a variety of allyl derivatives with excess *t*-BuHgCl under standard photostimulated conditions were kinetically 1st order in the allyl derivative. The observed rate constants gave a good correlation with σ_m of the leaving group substituent. The leaving group exerts an inductive effect on the energy of LUMO, which affects the rate of radical addition to the double bond of allyl derivatives.

The substituent and leaving group effects in the propargyl system are more complicated than those in the allyl system. The reaction mechanism is dependent upon the leaving group and bond dissociation energy of C-X (X is a central atom in the leaving group). The reaction of propargyl chloride and tosylate follow the mechanism described in Part I. With propargyl iodide and bromide, the dominant process shifts to halogen atom abstraction and leads to low yields of the substituted allene. α-Methylpropargyl chloride also undergoes predominant halogen atom abstraction with *t*-Bu•, but the corresponding tosylate undergoes addition of *t*-Bu• to the triple bond.

Experimental Section

General considerations

^{1}H NMR spectra were recorded on a Nicolet Magnetic Corp. NMC-1280 spectrometer (300 MHz) in DMSO-d_6. Product yields were determined by ^{1}H NMR spectroscopy integration with a known amount of biphenyl or by gas chromatographic analysis performed on a 3700 Varian Gas Chromatograph with a packed Chromosorb W (80-100 mesh) column coated with 7% OV-3 and a thermal conductivity detector. Product yields were determined by addition of a known amount of biphenyl or naphthalene as an internal standard.

t-BuHgCl and propargyl tosylate were prepared as previously described (see Part I). Allyl chloride, allyl bromide, allyltrimethylsilane, allylchlorodimethyl-silane, methallyl chloride, and propargyl chloride were purchased from Aldrich Chemical Company and used without further purification. Solvents were purchased and dried as mentioned before.

Determination of rate constants for the reactions of allyl and propargyl derivatives with *tert*-butylmercury chloride in the presence or absence of NaI

The allyl or propargyl derivative (0.5 mmol), *t*-BuHgCl (2.5 mmol) and the internal standard (0.5 mmol of biphenyl or benzene or dichloromethane) with or without NaI (2.5 mmol) were dissolved in 5 ml of nitrogen-purged deuterated DMSO. The solution was divided into ten NMR tubes (0.5 ml in each tube) each equipped with a rubber septum. After a 300 MHz ^{1}H NMR spectrum was obtained, the NMR tubes were irradiated at 35-40 °C with a 275 W sunlamp placed about 20 cm from the reaction

tube. Reaction tubes were removed at various times and the yield of the substitution product obtained from the integration of suitable protons.

The rate constant of the reaction was calculated according to the following equation by the linear regression method and the results are shown in Table 3-1.

$$-\ln (100 - \% \text{ yield of substituted product }) = k_{obs}\, t.$$

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PART IV. REACTIONS OF PROPARGYL IODIDE

Introduction

The species C_3H_3 was first detected by mass spectrometry from the pyrolysis of propargyl iodide at 1000-1100 °C.[1] The decomposition of propargyl iodide at 1000-1100 °C in either a high pressure or a low pressure reaction resulted in a good yield of the propargyl radical. The dimer, 1,5-hexadiyne, was also formed. The ionization potential of the propargyl radical is 57.9 ± 3.2 kcal / mol.

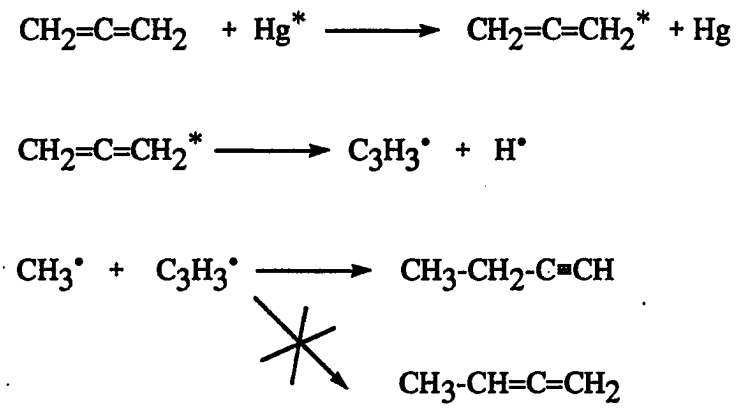
The propargyl radical has generally been considered to be a resonance hybrid of propargylic structure A and allenic structure B. Attempts to decide which structure most closely resembles the actual delocalized radical have been made based on both physical and chemical data.

$$HC{\equiv}CCH_2^{\bullet} \longleftrightarrow CH_2{=}C{=}CH^{\bullet}$$

A **B**

The Hg($^3p_1$) photosentized decomposition of allene leads to formation of a C_3H_3 radical.[2] Three products were produced by the mercury photosentized decomposition of allene: hydrogen, a radical of mass 39 (C_3H_3), and a substance of mass 78, evidently the dimer of this radical. The reaction of C_3H_3 • with added methyl radicals gave 1-butyne free of 1,2-butadiene. However, the C_3H_3 radical formed in the

direct photolysis of 1,3-butadiene was reported to couple with methyl radicals to give both 1-butyne and 1,2-butadiene.[3]



The ESR spectra of the propargyl radical trapped in solid matrices were reported by several workers.[4] However, under these conditions, lines were broad and the assignment of coupling constants was not straightforward. A well-resolved ESR spectrum of the C_3H_3 radical was generated during electron radiolysis of a solution of allene in propane by Fessenden and Schuler[5]; hyperfine constants of 18.9 and 12.6 Gauss for the CH_2 and CH groups were observed. Kochi and Krusic[6] also found that propyne and allene reacted with photochemically generated *t*-butoxy radical to produce the C_3H_3 radical. The six line spectrum is composed of a triplet of doublets with hyperfine constants of 18.92 and 12.68 Gauss for the CH_2 and CH groups. Spin densities have been related to coupling constants in delocalized radicals by use of the relationship $\alpha = Q\rho$ where α is the observed splitting, ρ is the spin density, and Q is the proportionality constant.[7] By use of $Q \cong 23$ G, the observed splitting constants give spin

densities of 0.82 and 0.55 for the CH_2 and CH group groups.[4d] However, these values may be distorted in the direction of too much spin density at the allenic terminus since it has been suggested[8] that Q is a function of the hybridization state of carbon with $Q_{sp} > Q_{sp2}$. To a first approximation, propargyl radical has sp^2 hybridization at the propargylic terminus and sp hybridization at the allenic terminus with cylindrical symmetry and unequal bond lengths.[9] Spin densities of 0.70 and 0.31 have been assigned from a matrix spectrum[4c] based on $Q_{sp2} = 23.7$ G and $Q_{sp} = 34.7$ G. Thus, although the exact values of spin densities are in doubt, ESR spectra demonstrated greater spin density on the methylene carbon atom (structure A).

The number of investigations of propargylic radicals generated by chemical rather than photochemical means are strictly limited. Walling and co-workers[10] studied the reaction of *tert*-butyl hypochlorite with a number of acetylenes and found the products to be essentially free of chloroallene. Poutsma and Kartch,[11] however, observed the formation of 3-chlorobutyne and 1-chloro-1,2-butadiene in the photochemical chlorination of 1-butyne with both molecular chlorine and *tert*-butyl hypochlorite.

Chlorination of either propyne or allene with *tert*-butyl hypochlorite gave propargyl chloride as a product;[12] the reactivity of the allenic hydrogen atoms in this case supports delocalization in the allenyl/propargyl radical. Reduction of propargyl bromide with tri-*n*-butyltin hydride gave both propyne and allene in a ratio of 5.25 : 1.[13]

Frantazier and Poutsma [14] have reported that the reduction reactions of substituted propargyl chlorides by tri-*n*-butyltin hydride produce mixtures of the corresponding acetylene and allene. However, even in cases where the allenic products were thermodynamic more stable, the acetylenic products were still favored kinetically. Acetylene / allene ratios in these reduction reactions varied from 1.4 to 20.

Pasto et al.[15] have reported the ROHF 4-31 G calculations of the propargyl radicals. The SOMO wave function ($C_1 = -0.890$, $C_2 = 0.067$, $C_3 = 0.0343$) indicates that the propargyl structure (A) is the most important resonance contributing structure.

In this Part, we will discuss the reaction of propargyl iodide with various organometallic reagents to produce C_3H_3 radicals and the dimerization products of C_3H_3 •.

Results and Discussion

The results with *t*-BuHgCl / *hv* demonstrated that *t*-Bu• attack upon $HC{\equiv}CCH_2I$ gives only traces of *t*-$BuCH{=}C{=}CH_2$, presumably because of Reaction 1-5 (page 23) leading to $HC{\equiv}CCH_2{\bullet} \leftrightarrow {\bullet}CH{=}C{=}CH_2$. We, therefore, examined the reactions of several other *tert*-butylating agents with propargyl iodide. Reaction in Et_2O with (*t*-$Bu)_2CuLi$ (at -78 or 0 °C) gave a mixture of C_6H_6 hydrocarbons as well as *t*-BuI, *t*-$BuCH_2C{\equiv}CH$, and $Me_3C\text{-}CMe_3$. However, only a trace of *t*-$BuCH{=}C{=}CH_2$ was found. A 72% yield of *t*-BuI was found in the reaction of equal molar quantities of (*t*-$Bu)_3ZnLi$ and $HC{\equiv}CCH_2I$ at 0 °C and again only a trace of allene could be detected. With (*t*-$Bu)_2Cu(CN)Li_2$ at 0 °C a good yield of *t*-$BuCH{=}C{=}CH_2$ was observed, but at -78 °C only a trace of the allene was observed and the product distribution resembled the reaction product from (*t*-$Bu)_2CuLi$.

The major C_6H_6 hydrocarbon formed was benzene. Smaller amounts of bipropargyl were found and a minor C_6H_6 isomer was detected by GCMS, but the retention time was too close to that of *t*-$BuCH_2C{\equiv}CH$ to allow GCIR identification. We find the formation of benzene to be surprising since the reaction of propargyl

bromide with Mg in THF is reported to give a mixture of bipropargyl, biallenyl, and propargylallene[16] or in Et_2O in the presence of CuCl to yield biallenyl and propargylallene exclusively.[17] We confirm the absence of benzene in the latter reaction although in our hands small amounts of bipropargyl were also formed. Reaction of *t*-BuHgCl / hυ or $(t\text{-Bu})_2CuLi$ with bipropargyl in Et_2O also failed to yield detectable amounts of benzene.

Photolysis of $HC{\equiv}CCH_2I$ in Et_2O formed bipropargyl and a dimeric compound $C_6H_6I_2$, but no benzene was detected. The bipropargyl could be formed by the coupling of two $HC{\equiv}CCH_2{\bullet}$ or by attack of $HC{\equiv}CCH_2{\bullet}$ upon the rearranged $CH_2{=}C{=}CHI$. Photolysis of *t*-BuHgCl in the presence of $HC{\equiv}CCH_2I$ in Et_2O produced bipropargyl, benzene, and a dimeric diiodide, although bipropargyl was now the major hydrocarbon. With 10 equiv of $HC{\equiv}CCH_2I$, the ratio of bipropargyl to benzene was 7:1, but with 0.5 equiv of $HC{\equiv}CCH_2I$, the ratio decreased to 3:1. Again reactions involving the rearranged $CH_2{=}C{=}CHI$ are a possibility. Photolysis of propargyl iodide and azobisisobutyronitrile in a 5:1 mol ratio also formed bipropargyl and benzene in 7:1 ratio and the dimeric diiodide was again detected.

The results obtained with propargyl iodide may not be pertinent to the mechanism of the reaction of propargyl chlorides with cuprate reagents. It is known that the stereospecific reactions of optically active alkyl chlorides with cuprates often lead to racemization with the corresponding alkyl iodides[18] and that cuprate reactions involving 5-hexenyl radical cyclization are more apt to occur with the hexenyl iodide than with the chloride.[19] Thus, perhaps electron transfer between $HC{\equiv}CCH_2I$ and the ate complexes leads to the formation of *t*-Bu• and the ensuing *t*-BuI, *t*-$BuCH_2C{\equiv}CH$, $Me_3C\text{-}CMe_3$, and C_6H_6 hydrocarbons.

It seems certain from the relative reactivity data reported in Part II and the product data reported in this Part, that the reaction of $(t\text{-Bu})_2Cu(CN)Li_2$ with either $HC{\equiv}CCH_2Cl$ or $HC{\equiv}CCH_2I$ at 0 °C can proceed by a process not involving the intermediacy of *t*-Bu•. The result with $(t\text{-Bu})_2Cu(CN)Li_2$ illustrate a rather dramatic effect of temperature upon mechanism in that at 0 °C the reaction with $HC{\equiv}CCH_2I$ yields $t\text{-BuCH=C=CH}_2$ by a process not involving *t*-Bu• , but at −78 °C the radical coupling process dominates and more $t\text{-BuCH}_2C{\equiv}CH$ than $t\text{-BuCH=C=CH}_2$ is observed.

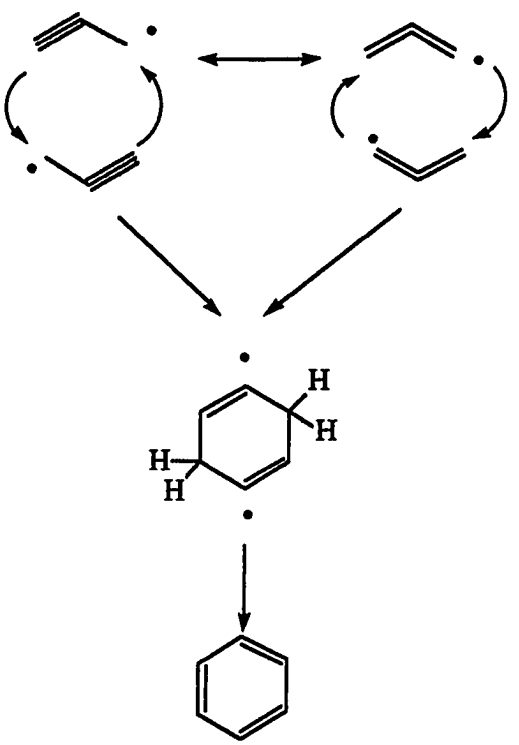
At present, we see no other way to explain the formation of benzene in the reactions of $HC{\equiv}CCH_2I$ except by the coupling of two C_3H_3 radicals, possibly complexed with Cu or Hg. One possible pathway is a cyclodimerization leading to a cyclohexadiene-1,4-diyl which rearrange to benzene. Pyrolysis of dipropargyl oxalate at 600-660 °C yields benzene as the predominant product,[20] but bipropargyl is known to form benzene and fulvene at 380 °C,[21] although at lower temperatures only 3,4-dimethylenecyclobutene is produced.[22]

There are two possible resonance structures for C_3H_3 radical, one is propargyl radical and the other is π-allenyl radical. Both of them can dimerize to form the 1,4-cyclohexadiene-1,4-diyl which rearranges to benzene as shown in Scheme 4-1. The π-propargyl and the σ-allenyl radicals may be discrete entities. Either of them could dimerize to form the 1,4-cyclohexadiene-1,4-diyl which rearranges to benzene.

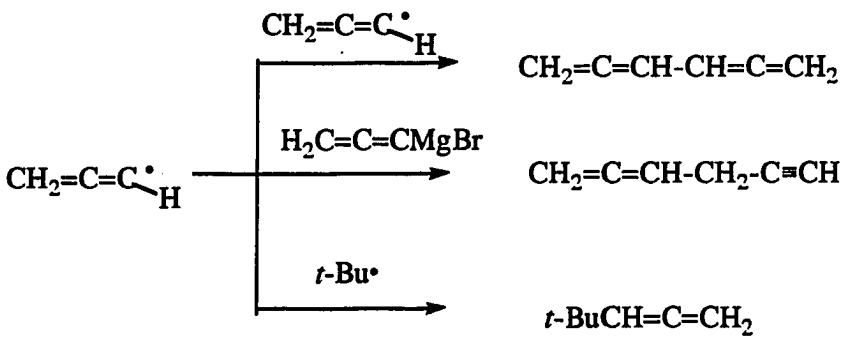
In an attempt to distinguish between these two processes, we prepared $H_2C{=}C{=}CHMgBr$[23] , by the reaction of propargyl bromide with Mg in diethyl ether solution. Reaction with $(t\text{-Bu})_2CuLi$ at -78 °C or 0 °C gave a mixture of $(H_2C{=}C{=}CH)_2$, $H_2C{=}C{=}CH\text{-}CH_2\text{-}C{\equiv}CH$, $t\text{-BuHC=C=CH}_2$, and $Me_3C\text{-}CMe_3$. The $(H_2C{=}C{=}CH)_2$ is the major product and no benzene is detected. This reaction possibly involves the

localized allenyl radical. The possible pathways to the observed products are shown in Scheme 4-2. The biallenyl was obtained by coupling the two allenyl radicals, propargyl-allene was obtained by the attack of the allenyl radical upon the $H_2C{=}C{=}CHMgBr$[23] and the *t*-$BuHC{=}C{=}CH_2$ was formed by coupling the *t*-butyl radical with the allenyl radical.

Scheme 4-1



Scheme 4-2



Photolysis of $H_2C{=}C{=}CHHgBr$ in DMSO by a sunlamp at 35-40 °C did not give benzene. However, the reaction of $H_2C{=}C{=}CHHgBr$ with $(t\text{-Bu})_2CuLi$ at -78 °C in ether solution formed biallenyl and benzene in a 7: 1 ratio.

From the above discussion, the propargyl radical appears to be responsible for the formation of benzene in the reaction of propargyl iodide with $(t\text{-Bu})_2CuLi$. However, the reaction of 1-iodo-2-butyne ($CH_3C{\equiv}CCH_2I$) with *t*-BuHgCl / hυ in DMSO or with $(t\text{-Bu})_2CuLi$ at -78 °C in diethyl ether solution gave a mixture of C_8H_{10} hydrocarbons, but none of the xylenes were observed. The allene $t\text{-BuC}(CH_3){=}C{=}CH_2$ can also not detected. Possibly the methyl substituent effect, increases the energy of the LUMO of the triple bond, so that radical addition to the triple bond is more difficult and only the coupling products are observed.

We have been unable to completely identify the source of benzene in the reactions of propargyl iodide. However, some generalities can be made. In general, $CH_2{=}C{=}CHMBr$ (M = Mg or Hg) reacts under conditions where radicals may be present to form mainly biallenyl and relatively small amounts of bipropargyl or benzene. Benzene formation was most significant in the reactions of *tert*-butylcuprates or *t*-

BuHgCl / hυ with propargyl iodide. In these reactions very little biallenyl is produced and the benzene is accompanied by a variable amount of bipropargyl. Possibly species such as $HC{\equiv}CCH_2M$ (M = Cu (I), Hg(I)) are precursors to the postulated 1,4-cyclohexadiene-1,4-diyl. Reactions involving unstable $(HC{\equiv}CCH_2)_2M$ are also a possibility.

Conclusion

The reaction of *t*-BuHgCl with propargyl iodide under sunlamp irradiation gives evidence of *t*-Bu• attack upon $HC{\equiv}CCH_2I$ to form C_3H_3• which can cyclodimerization to form benzene or couple to form bipropargyl. Benzene was the major C_6H_6 hydrocarbon formed from $HC{\equiv}CCH_2I$ with $(t\text{-Bu})_2CuLi$ at -78 or 0 °C.

The reaction of $(t\text{-Bu})_2CuLi$ with $HC{\equiv}CCH_2I$ seems to involve *t*-Bu• at -78 or 0 °C. The reaction of $(t\text{-Bu})_2Cu(CN)Li_2$ with $HC{\equiv}CCH_2I$ shows a rather dramatic effect of temperature upon mechanism; *t*-Bu• is not involved at 0 °C, while the reaction proceeds by a process involving *t*-Bu• at -78 °C.

The reactions of $CH_3C{\equiv}CCH_2I$ with $(t\text{-Bu})_2CuLi$ or *t*-BuHgCl / hυ formed neither $t\text{-BuC}(CH_3){=}C{=}CH_2$ nor xylene.

Experimental Section

General considerations

^1H NMR spectra were recorded on a Nicolet Magnetic Corp. NMC-1280 spectrometer (300 MHz) in DMSO-d_6. Product yields were determined by ^1H NMR integration with a known amount of biphenyl or gas chromatographic analysis was

performed on a 3700 Varian gas chromatograph with a packed Chromosorb W (80-100 mesh) column coated with 7% OV-3 and a thermal conductivity detector. Product yields were determined by addition of a known amount of biphenyl or naphthalene as an internal standard.

t-BuHgCl and propargyl iodide were prepared as previously described (see Part I). 1,5-Hexadiyne was purchased from Alfa Products. AIBN was purchased from Aldrich Chemical Company and used without further purification. Solvents were purchased and dried as mentioned before. $(t\text{-Bu})_2Cu(CN)Li_2$ and $(t\text{-Bu})_2CuLi$ were prepared as previously described (see Part II).

Preparation of allenyl derivatives

Allenylmagnesium bromide[23] Propargyl bromide (3 mmol) , which was dissolved in 10 ml dry ether, was added dropwise to a solution of Mg (3 mmol), a trace of $HgCl_2$, and dry ether (20 ml) at 0°C under nitrogen with stirring. After formation of the Grignard reagent, the ice bath was removed. The solution was stirred until the Mg disappeared.

Allenylmercury bromide[24] Propargyl bromide (0.4 ml) was added to a mixture of ether (15 ml) and Mg (0.5 g) which contained a trace of $HgCl_2$. After the reaction started, the rest of the propargyl bromide, dissolved in 35 ml dry ether, was added to the mixture dropwise at 0 °C or below. More propargyl bromide was added until all the Mg reacted. $HgCl_2$ (34 mmol) dissolved in dry THF was then added to the solution. After additional stirring for 3 h, the reaction mixture was quenched by 6.6% aqueous NH_4NO_3 solution (80 ml) and ether (100 ml) at 0°C. The ether layer together with ethereal extracts of the aqueous layer were dried with Na_2SO_4. Evaporation of the solvent gave a product which was recrystallized from the mixed solvents of

dichloromethane and hexane to give material of mp 86-88 °C; ^{1}H NMR ($CDCl_3$) δ 5.26 (t, J = 7 Hz, 1 H); 4.71 (d, J = 7 Hz, 2 H); GCMS *m /z* (relative intensity) : 324 (2), 322 (8), 321 (3), 320 (12), 319 (8), 318 (8), 317 (4), 316 (3), 283 (4), 282 (9), 281 (9), 280 (37), 279 (28), 278 (34), 277 (29), 276 (17), 275 (4), 243 (4), 242 (2), 241 (15), 250 (14), 239 (16), 238 (15), 237 (10), 236 (3), 204 (4), 203 (2), 202 (18), 201 (8), 200 (15), 199 (18), 198 (6), 120 (45), 119 (9), 118 (49), 77 (39), 76 (11), 75 (9), 74 (16), 63 (17), 62 (6), 52 (100), 51 (74), 50 (45); high resolution mass spectrum : $C_3H_3Hg^{198}Br^{79}$ is calculated as 315.90886 and measured as 315.90287. IR (neat) : 3300 (v. weak), 3009 (v. weak), 2980 (v. weak), 1928 (strong), 1647 (v. weak), 1416 (v. weak), 1406 (v. weak), 1165 (medium), 1047 (weak), 1022 (weak), 833 (medium), 810 (weak).

1,2,4,5-Hexatetraene[23] To H_2C=C=CHMgBr, prepared as previously described, 0.2 g portion of finely pulverized, dry copper(I) chloride was added. The mixture which became a chocolate brown color after 2-3 min, was stirred for 15 min at room temperature and cooled to 5 °C. Stirring was continued while a solution of propargyl bromide (3.5 mmol) in 5 ml of dry ether was added at a rate such that the internal temperature was kept at ca. 20°C. The mixture became almost black, and two phases were discernible when stirring was stopped, especially toward the end of the addition. The cooling bath was removed, and stirring continued for 15 min at room temperature to complete the dimerization.

Preparation of 1-iodo-2-butyne[25]

A mixture of 33 ml (0.12 mol) of triphenylphosphite and 12 ml (0.20 mol) of methyl iodide was heated to reflux for 12 h. The temperature was maintained at 150 °C. Formation of the complex, $(PhO)_3PMeI$, was confirmed by ^{1}H NMR [δ 3.15 (d, 3H,

J = 16 Hz, CH_3), 7.50 (s, 15 H, C_6H_5)]. Methylene chloride (68 ml) was added to the cooled crude (PhO)$_3$PMeI complex to make a solution which was then cooled in an ice bath. To this solution, 7.0 g (0.1 mole) of 2-butyn-1-ol was added dropwise with stirring. The reaction mixture was then stirred at 0 °C for an additional 6 hours. The methylene chloride was removed under reduced pressure, and the product distilled at 2 mm Hg into an acetone-dry ice cooled trap and then dried ($MgSO_4$). The product was confirmed by ^{1}H NMR.[19] ^{1}H NMR ($CDCl_3$) δ 1.85 (t, 3H, J = 3 Hz, CH_3), 3.65 (q, 2H, J = 3 Hz, CH_2I).

The reaction of propargyl iodide with *tert*-butylating agents

The cuprate complexes , [(*t*-Bu)$_2$CuLi, (*t*-Bu)$_2$Cu(CN)Li$_2$, and (*t*-Bu)$_3$ZnLi], were prepared as described before. After the cuprate complex was freshly prepared, 1 mmol of propargyl iodide was added dropwise over a period of 1 min at -78 °C and the resulting solution was stirred at -78 or 0 °C for 30 min. After hydrolysis with 1ml of saturated aqueous ammonium chloride, the mixture was then added to ice water. The mixture was extracted by ether twice, washed with cold water twice, and dried over Na_2SO_4. The ether was removed carefully by distillation at room temperature. The concentrated ether solution was analyzed by GLC, GCMS, and GCIR. Blank experiments in the absence of propargyl iodide showed the complete absence of benzene in the final extract.

Benzene was identified by GC retention time, GCMS and by GCIR, which matched the reported values.[26] Other products were identified by GCMS and GCIR.

4,4-Dimethyl-1-pentyne: GCMS *m /z* (relative intensity) 81 (61), 79 (12), 57 (100), 53 (11), 41 (55), 39 (21), 29 (39).

GCIR (relative intensity) 3329 (44), 2966 (100), 2122 (12), 1481 (20), 1373 (24), 1238 (28), 732 (10) cm^{-1}.

1,5-Hexadiyne: GCMS *m /z* (relative intensity) 78 (17), 77 (87), 76 (18), 74 (13), 63 (8), 52 (68), 51 (46), 39 (100), 38 (24).

GCIR (relative intensity) 3336 (100), 3325 (99), 2939 (22), 2133 (7), 1439 (10), 1338 (7), 1261 (42), 1072 (3), 937 (6), 825 (3) cm^{-1}. The IR spectrum matched that reported previously.[27]

4,4-Dimethyl-1,2-pentadiene : GCMS *m /z* (relative intensity) 96 (25), 81 (72), 79 (30), 57 (100), 53 (32), 4 (85), 39 (52), 29 (53), 27 (34).

An unidentified C_6H_6 hydrocarbon whose GC retention time was close to that of 4,4-dimethyl-1-pentyne was also observed: GCMS *m /z* (relative intensity) 78 (100), 77 (45), 76 (10), 74 (9), 63 (8), 56 (12), 52 (71), 51 (45), 50 (40), 42 (14), 41 (13), 39 (45), 38 (13).

<u>The photostimulated reaction of propargyl iodide in ether solution</u>

A solution of propargyl iodide(80 % pure, the main contaminant was the isomeric allenyl iodide) in ether (1 ml) was sealed in a 5 mm NMR tube. Then, the mixture was photolyzed with a sunlamp ca. 20 cm from the tube for 24 h. The mixture was analyzed by GLC, GCMS, and ^1H NMR spectroscopy. The mixture contained bipropargyl, a dimeric compound $C_6H_6I_2$ and starting material. No benzene was detected.

Bipropargyl was identified by its GC retention time, and GCMS which matched those of the authentic compound.

Dimeric compound $C_6H_6I_2$: GCMS *m /z* (relative intensity) 332 (4), 293 (2), 254 (2), 205 (2), 166 (2), 165 (2), 127 (4), 78 (100), 77 (11), 52 (17), 51 (22), 50 (13), 39 (48), 38 (12).

The photostimulated reaction of propargyl iodide with *t*-BuHgCl in ether solution

A mixture of propargyl iodide and *t*-BuHgCl (5 mmol / 0.5 mmol or 1 mmol / 2 mmol) was dissolved in 1 ml of dry ether in a 5 mm NMR tube equipped with a plastic cap sealed with teflon tape. The mixture was irradiated with a 275 W sunlamp ca. 20 cm from the tube for 24 h. The red precipitate, HgI_2, was observed. The mixture was analyzed by GLC, GCMS. Bipropargyl, the dimeric compound $C_6H_6I_2$ and benzene were found in the mixture. The ratio of bipropargyl to benzene was determined by ^1H NMR spectroscopy. With 10 equiv of $HC{\equiv}CCH_2I$, the ratio of bipropargyl to benzene was 7:1, but with 0.5 equiv of $HC{\equiv}CCH_2I$, the ratio of bipropargyl to benzene decreased to 3:1.

The photostimulated reaction of propargyl iodide with AIBN in ether solution

Propargyl iodide (0.5 mmol) and AIBN (0.1 mmol) were dissolved in 1 ml of dry ether in a 5 mm NMR tube equipped with a plastic cap sealed with teflon tape. The mixture was irradiated with a 275 W sunlamp ca. 20 cm from the tube for 24 h. The mixture was analyzed by GLC, GCMS. Bipropargyl and benzene were found in the mixture. The compounds were identified by comparison with the authentic compound. The ratio of bipropargyl to benzene was 7:1 as determined by ^1H NMR spectroscopy.

The reaction of 1-iodo-2-butyne with $(t\text{-Bu})_2CuLi$

The cuprate complex, (*t*-Bu)$_2$CuLi (1 mmol), was prepared as described before. After the cuprate complex was freshly prepared, 1 mmol of $CH_3C{\equiv}CCH_2I$ was

added dropwise over a period of 1 min at -78 °C and the resulting solution was stirred at -78 or 0 °C for 30 min. After hydrolysis with 1ml of saturated aqueous ammonium chloride, the mixture was then added to ice-water. The mixture was extracted by ether twice, washed with cold water twice, and dried over Na_2SO_4. The ether was removed carefully by distillation at room temperature. The concentrated ether solution was analyzed by GLC, GCMS, and GCIR.

A mixture of C_8H_{10} hydrocarbons was found. The ^1H NMR spectroscopy of the mixture did not show any aromatic proton. The GCMS, GCIR spectra of these C_8H_{10} mixture did not match those of para- or ortho-xylene. The GCMS, GCIR spectra were not sufficient to identify these compounds. We believe they are not products of cyclodimerization.

The photostimulated reaction of 1-iodo-2-butyne with *t*-BuHgCl in ether or DMSO solution

1-Iodo-2-butyne (0.1 mmol) and *t*-BuHgCl (0.5 mmol) were dissolved in 1 ml of dry ether or DMSO-d_6 in a 5 mm NMR tube equipped with a plastic cap sealed with teflon tape. The mixture was irradiated with a 275 W sunlamp ca. 20 cm from the tube for 24 h. The mixture was analyzed by GLC, GCMS, or ^1H NMR spectroscopy. No aromatic protons were shown by ^1H NMR spectroscopy and no xylene was detected by GCMS.

The photostimulated reaction of 1,2,4,5-hexatetraene with *t*-BuHgCl in ether solution

1,2,4,5-Hexatetraene was prepared as described before. The *t*-BuHgCl (5 mmol) was added to 1,2,4,5-hexatetraene (1 mmol) in 10 ml of ether in a Pyrex tube equipped

with a septum sealed with teflon tape. The mixture was irradiated with a 275 W sunlamp ca. 20 cm from the tube for 24 h. The mixture was analyzed by GLC, GCMS, or ^1H NMR spectroscopy. No benzene was detected, although the concentration of the starting material had decreased.

The reaction of allenylmagnesium bromide with (*t*-Bu)$_2$CuLi

An ether solution of $H_2C{=}C{=}CHMgBr$ (3 mmol), prepared freshly as described before, was added dropwise to the solution of freshly prepared (*t*-Bu)$_2$CuLi (3 mmol) in ether at -78 °C. After addition was complete, the solution was stirred for another 30 min at -78 or 0 °C. After hydrolysis with 1ml of saturated aqueous ammonium chloride, the mixture was then added to ice-water. The mixture was extracted with ether twice, washed with cold water twice and dried over Na_2SO_4. The ether was removed carefully by distillation at room temperature. The concentrated ether solution was analyzed by GLC, GCMS, and GCIR. Biallene was found as a major product. Propargylallene and a trace of *tert*-butylallene were also detected. These products were identified by the GCMS, GCIR and by comparison with the authentic compounds. No benzene was detected.

The reaction of allenylmercury bromide with (*t*-Bu)$_2$CuLi

A solution of $H_2C{=}C{=}CHHgBr$ (1 mmol) in 10 ml of dry ether was added dropwise to the solution of freshly prepared (*t*-Bu)$_2$CuLi (1 mmol) at -78 °C. After the addition was complete, the solution was stirred for another 30 min at -78 °C. After hydrolysis with 1ml of saturated aqueous ammonium chloride, the mixture was then added to ice-water. The mixture was extracted by ether twice, washed with cold water twice, and dried over Na_2SO_4. The ether was removed carefully by distillation at room

temperature. The concentrated ether solution was analyzed by GLC, GCMS, and GCIR. Biallene was found to be major product and benzene was detected. The ratio of biallene to benzene was 7:1 as determined by ^{1}H NMR spectroscopy. These products were identified by GCMS, GCIR and by comparison with the authentic compounds.

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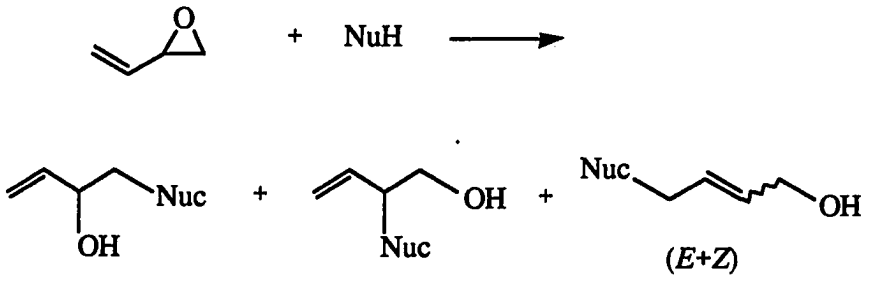
PART V. THE REACTIONS OF VINYLIC EPOXIDES WITH ORGANOMERCURIALS

Literature Review

Introduction

Nucleophilic and organometallic additions to vinylic epoxides have become useful synthetic methods, when the stereochemistry of the products can be controlled. However, many of these reactions are not regioselective; mixtures of 1,2-addition and 1,4-addition products are formed. The 1,4-addition product is also generally produced as a mixture of *E* and *Z* isomers (Eq. 5-1).

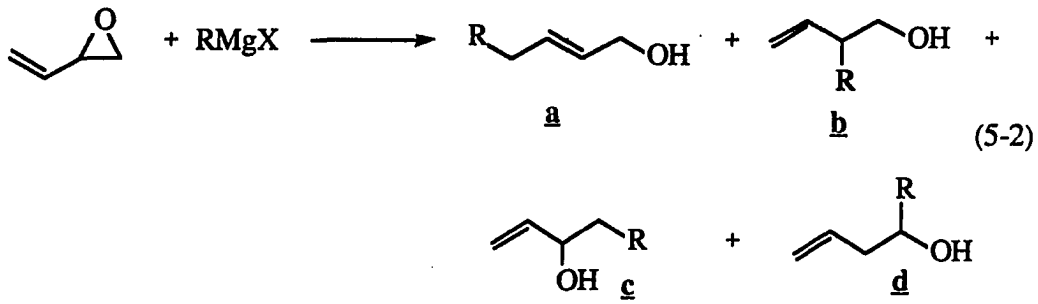


(5-1)

In this review, the reactions of vinylic epoxides with organometallic nucleophiles will be discussed. The organometallic nucleophiles are organomagnesium, -lithium, -borane reagents and palladium(0) catalyzed reactions.

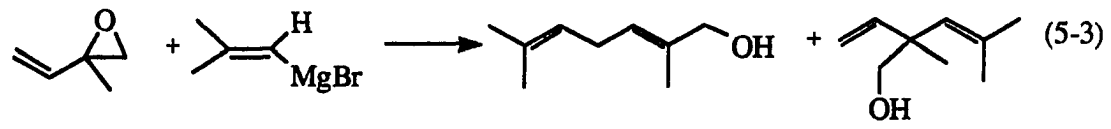
Reactions of organometallic nucleophiles to vinylic epoxides

Organomagnesium compounds Alkyl and aryl Grignard reagents were the first organometallic nucleophiles to be reacted with butadiene monoepoxide.[1]



(5-2)

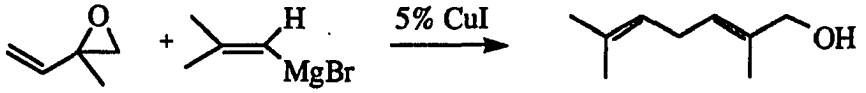
It was reported that the 1,4-addition product a was the only product. However, closer examination of the reaction revealed that mixtures of alcohol a-d were obtained.[2] The ratio of products is dependent upon the Grignard reagent. However, the reactions of Grignard reagents, in the presence of a catalytic amount of copper halide, gives a good yield of the 1,4-addition product.[3]



(5-3)

32% 19%

(20 : 80 *E* / *Z*)

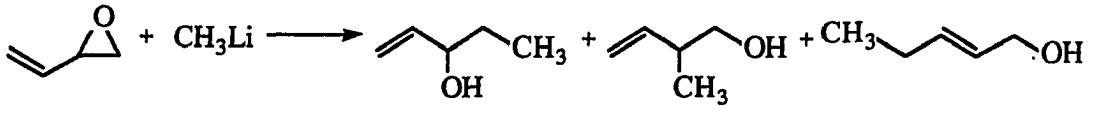


(5-4)

79%

(96 : 4 *E* / *Z*)

Organolithium reagents Organolithium reagents react with butadiene monoxide to get mixtures of products (Eq. 5-5).[2f,2g] The ratio of products depends upon the organolithium reagent and the conditions of the reaction.



(5-5)

17 : 63 : 20

(1.1: 1 *E* / *Z*)

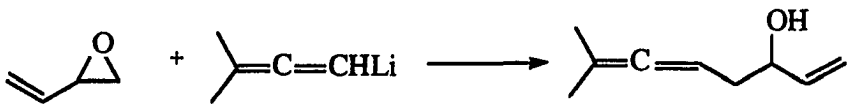
When 3-methyl-3,4-epoxy-1-butene was allowed to react with organolithium reagents, the 1,4-addition product was formed exclusively, as a mixture of stereoisomers [2h,4] (Eq. 5-6).

(5-6)

97%

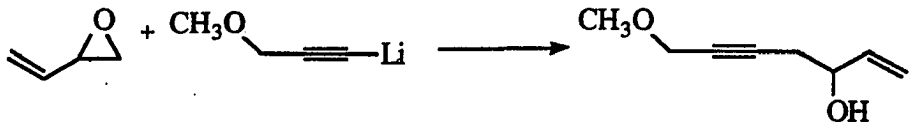
(16 : 84 *E* / *Z*)

Blame et al.[5] have found that the reactions of allenyl or alkynyllithium compounds with butadiene monoepoxide generally give products which resulting from attack of the organolithium species on the unsubstituted carbon of the ring of the vinylic epoxide (Eqs. 5-7 and 5-8). In contrast to acyclic vinylic epoxides, the cyclic vinylic epoxides give 1,2-addition products only.[6]



(5-7)

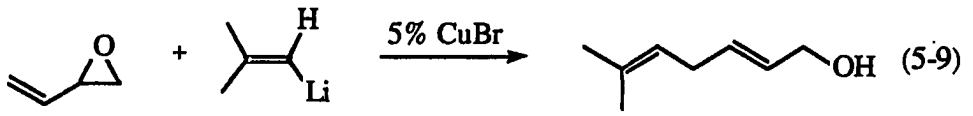
77%



(5-8)

70%

Just as with organomagnesium reagents, the reactions of vinylic epoxides and organolithium compounds catalyzed by copper halide produced allylic alcohols, predominantly as the *E*-isomer (Eq. 5-9).[3a]



(5-9)

94%

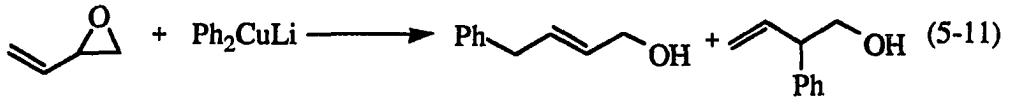
(88 :12 *E* / *Z*)

Tamura and co-workers have reported that acylic vinylic epoxides reacted with alkyllithium reagents in the presence of a base, such as tertiary amine or lithium alkoxide (Eq. 5-10), to give regio- and stereoselectively the allylic alcohol.[7]

(5-10)

no base 76% (12 : 88 *E* / *Z*)
1 equiv *n*-BuOLi 73% (3 : 97 *E* / *Z*)

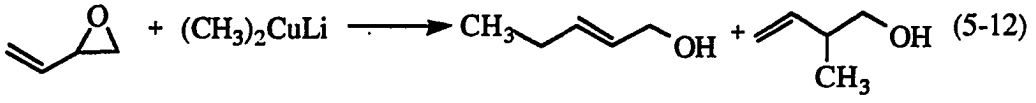
<u>Organocopper reagents</u> Organocopper reagents have been proven to be superior reagents for the formation of allylic alcohols from vinylic epoxides. It was found that organocuprate reagents would add to vinylic epoxides predominantly in a 1,4-fashion to yield the corresponding E-allylic alcohols with a degree of stereoselectivity (Eqs. 5-11 and 5-12).[2e,2f]



(5-11)

85 : 15

(90 : 10 *E* / *Z*)



(5-12)

94 : 6

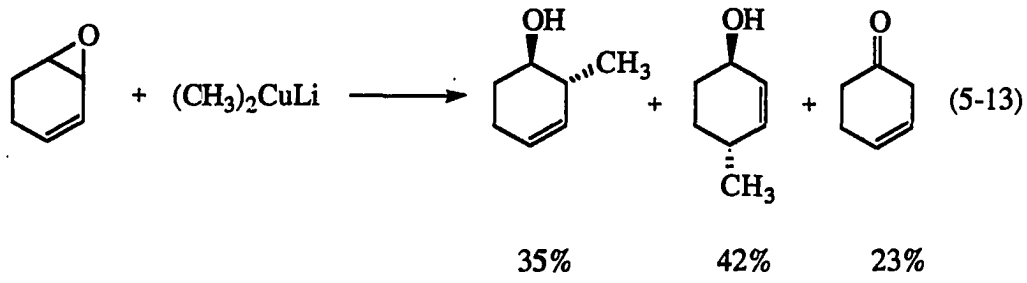
(3.8 : 1 *E* / *Z*)

Mechanistic aspects of these reactions have been studied recently.[8] Lipshutz and co-workers have found that nearly the same results as those shown in equation 5-11 and 5-12 were obtained, when $R_2Cu(CN)Li_2$ was allowed to react with 3-methyl-3,4-epoxy-1-butene.[9]

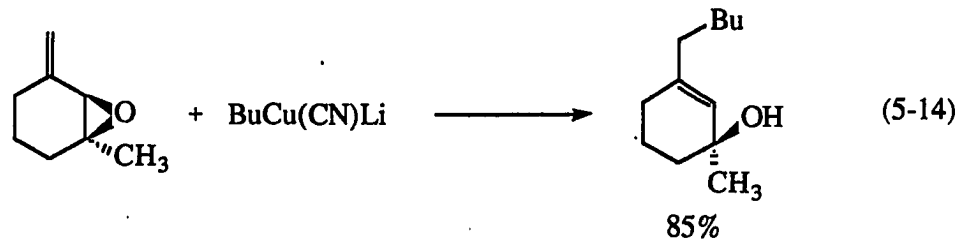
Ghribi [10]and Alexakis [11] have found that they were able to control the regio- and stereoselectivity of the reaction of 3-methyl-3,4-epoxy-1-butene with alkylcopper reagents. The E-isomer of the allyl alcohol was formed quantitatively in the presence of one equivalent of boron trifluoride etherate.

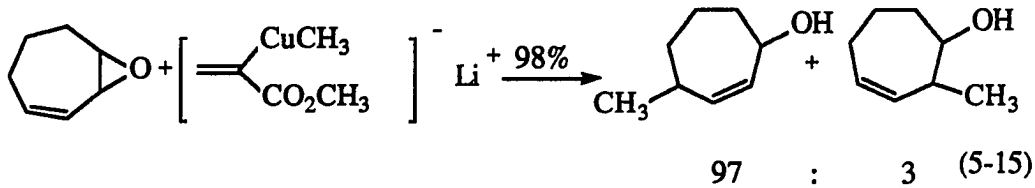
Johnson and Dhanoa have studied the reactions of vinylic epoxides with organocuprates of the type $(CH_3SOCH_2CuR)Li$.[12] They found that allylic alcohols were obtained exclusively as the E-isomer from these reactions.

Unlike the additions of organocuprate reagents to acylic vinylic epoxides, the reactions with cyclic vinylic epoxides yield a significant amount of 1,2-addition product (Eq. 5-13).[13]

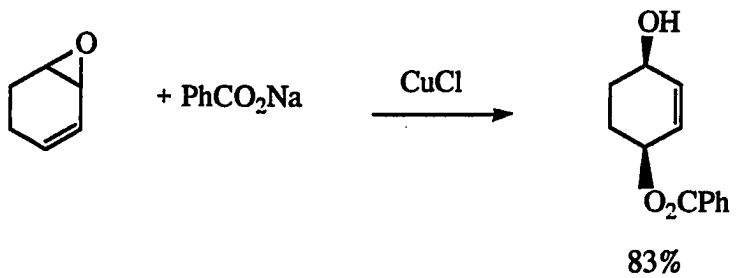


Marino and co-workers have found that mixed cyano- and (1-carbomethoxyvinyl) cuprates reacted with cyclic vinylic epoxides with excellent results (Eqs. 5-14 and 5-15).[14]



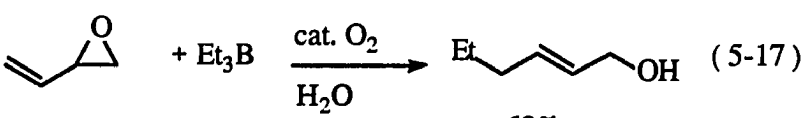


Marino and Jaen also found a mild method for the 1,4-syn opening of certain vinylic epoxides, using sodium carboxylates in the presence of cuprous chloride (Eq. 5-16).[15]



83% (5-16)

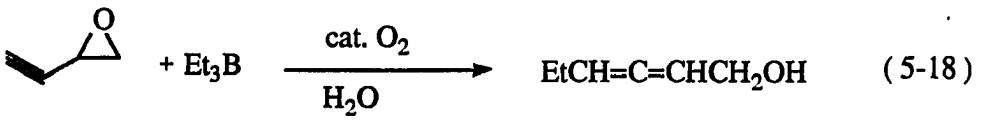
Organoboron reagents It has been shown that alkylboranes will undergo 1,4-additions to butadiene monoepoxide (Eq. 5-17).[16]



68% (5-17)

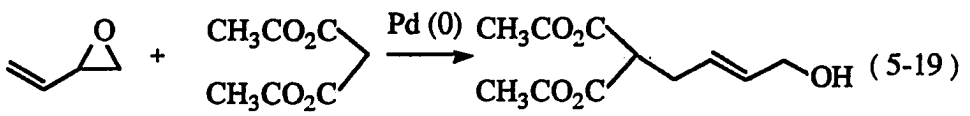
(88 : 12 *E* / *Z*)

This reaction is believed to occur via a free radical chain mechanism. Trialkylboranes will also undergo additions to ethynyl epoxides to produce the corresponding allenic alcohols.[17]



(5-18)

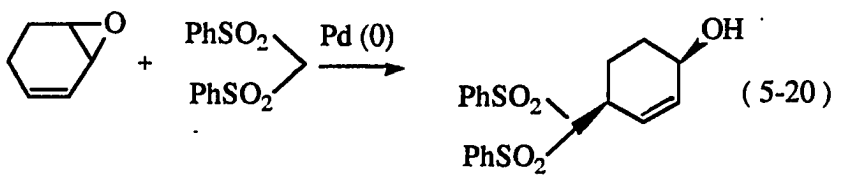
Palladium(0) catalyzed reaction Trost and Molander[18] and Tsuji[19] et al. independently reported that vinylic epoxides react with stabilized carbon nucleophiles in the presence of a catalytic amount of palladium(0) to produce allylic alcohols in good yields (Eqs. 5-19~ 5-22). These reactions are generally highly regio- and stereoselective.



(5-19)

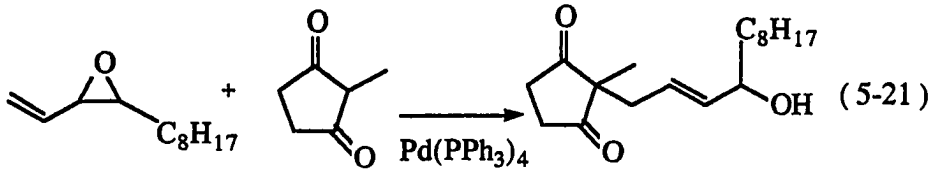
75%

(5:1 *E* / *Z*)



(5-20)

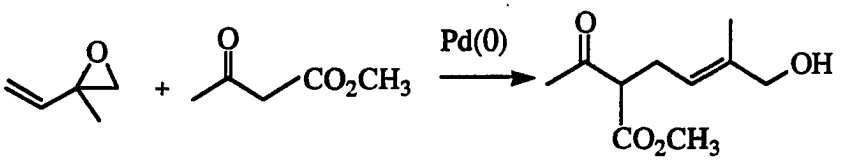
85%



(5-21)

91%

(98:2 *E* / *Z*)

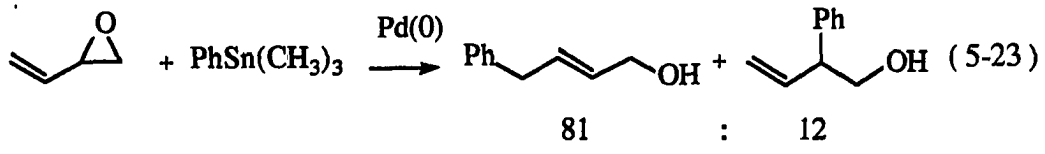


(5-22)

62%

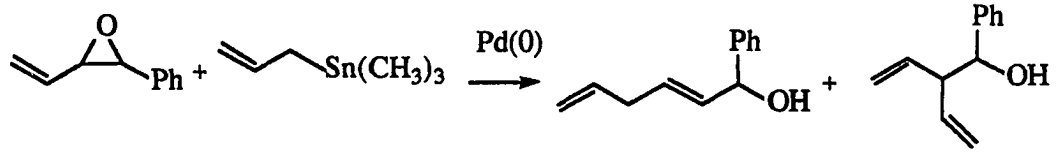
(5:2 *E* / *Z*)

Echavarren and co-workers have recently reported that vinylic epoxides reacts with organostannanes in the presence of a catalytic amount of palladium(0) to yield the desired product as a mixture of regio- and stereoisomers (Eqs. 5-23~24).[20]



81 : 12 (5-23)

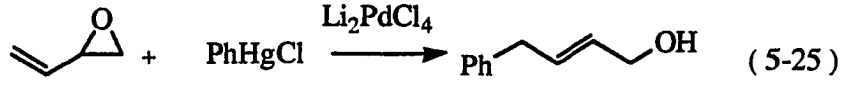
(18: 1 *E*/*Z*)



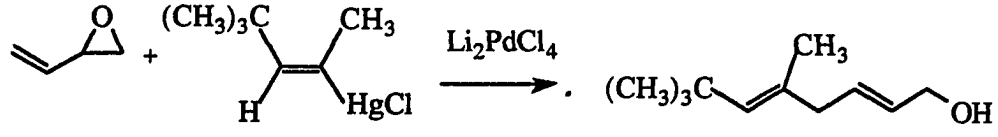
98 : 2 (5-24)

(10:1 *E*/*Z*)

Larock and Ilkka have reported that vinylic epoxides react with aryl- and vinylmercurials in the presence of a stoichiometric amount of palladium(II) (Eqs. 5-25, 26).[21]



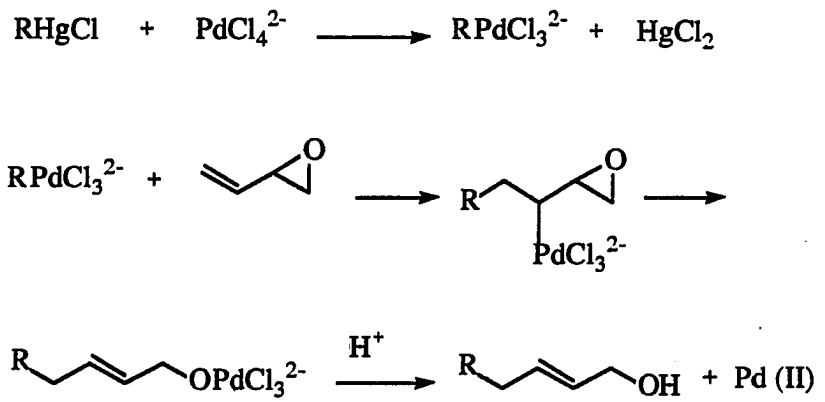
76% (*E* only) (5-25)



81% (89 : 11 *E*/*Z*) (5-26)

The mechanism has been proposed as shown in Scheme 5-1.

Scheme 5-1



Conclusion

There are a large number of nucleophilic additions to vinylic epoxides reported in the literature. Many of these reactions are regio- and stereoselective. Organocuprates are superior reagents for forming allylic alcohols regio- and stereoselectively from the corresponding vinylic epoxides. The 1,4-addition of nucleophiles to vinylic epoxides always forms the allylic alcohol as the final products. Even in the presence of a base, the allylic alcohol was the final product in the reaction of *n*-butyllithium with 1,3-butadiene epoxide.[7] The reaction of 1,3-butadiene epoxide with a trialkylboranes is believed to proceed via a free-radical mechanism to yield the allylic alcohol.

The Reactions of Vinylic Epoxides

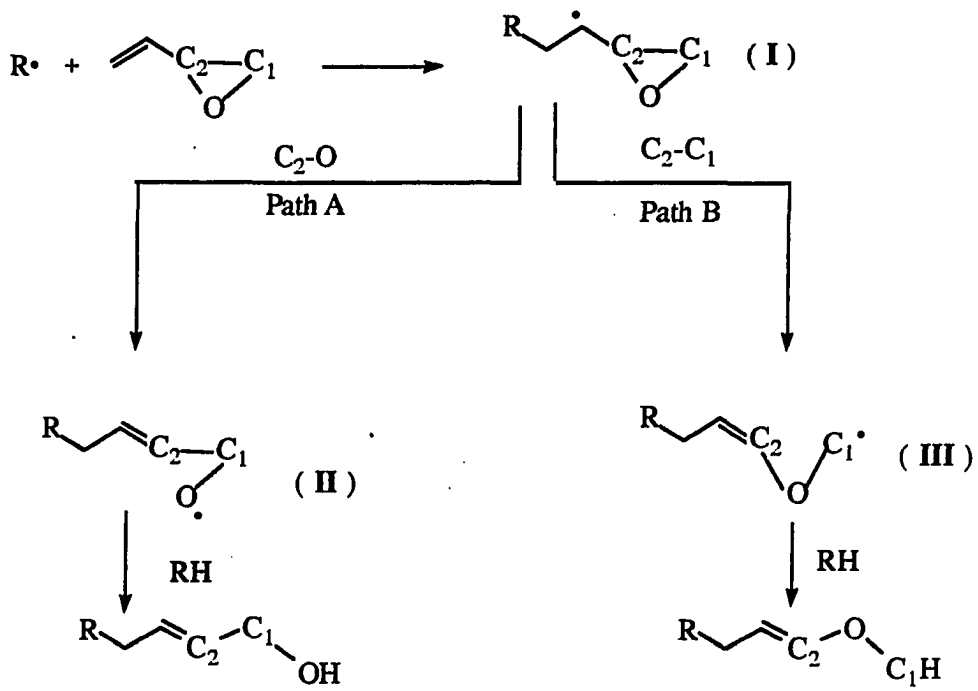
Introduction

The ring opening reactions of oxiranes by ionic or free radical mechanisms occur characteristically via severance of a carbon-oxygen bond. Opening of the ring at the carbon-carbon bond has been rarely reported.[22] The generation of a radical on a carbon α to an oxirane ring, either by a hydrogen abstraction process or by radical addition to a vinyl oxirane has been observed to lead to the formation of allylic alcohols. These types of products are formed as a consequence of homolytic scission of the C_2-O bond according to Path A in the Scheme 5-2.

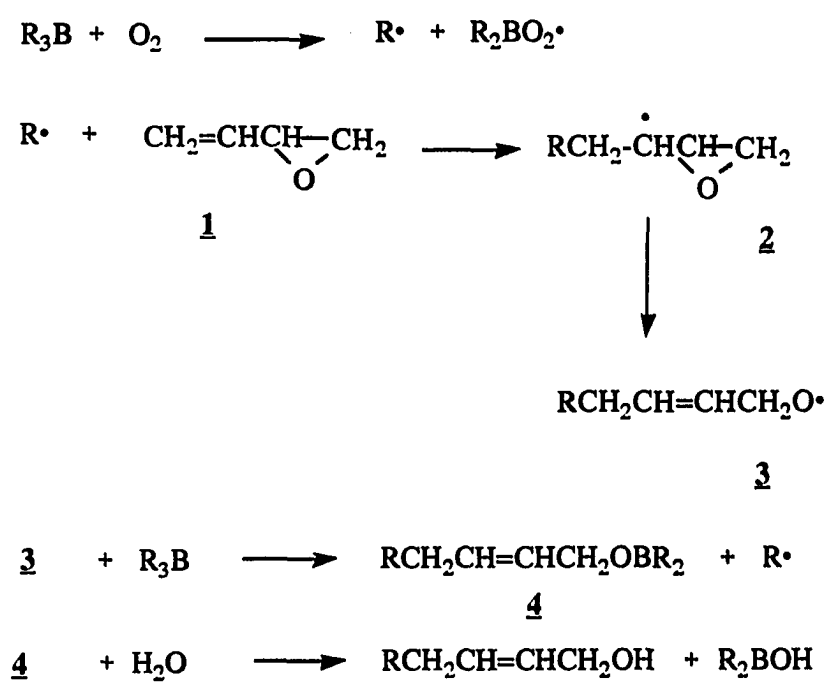
On the basis of the known stabilities of oxygen and carbon radicals, elimination via Path B should be thermodynamically less important than Path A, particularly when the oxirane ring is in a terminal position so that the resulting intermediate III would be a primary radical.

Brown et al.[16] have reported that 1,3-butadiene epoxide reacted with trialkylboranes in the presence of catalytic amounts of oxygen or other free radical initiators to give the corresponding allylic alcohols (Eq. 5-18). The free radical mechanism of Scheme 5-3 was proposed.

Scheme 5-2


R• +
C2—C1
O
R
C2—C1
O
(I)
C2-O
Path A
C2-C1
Path B
R
C2—C1
O
(II)
RH
R
C2
C1
OH
R
C2
C1
O
(III)
RH
R
C2
O
C1H

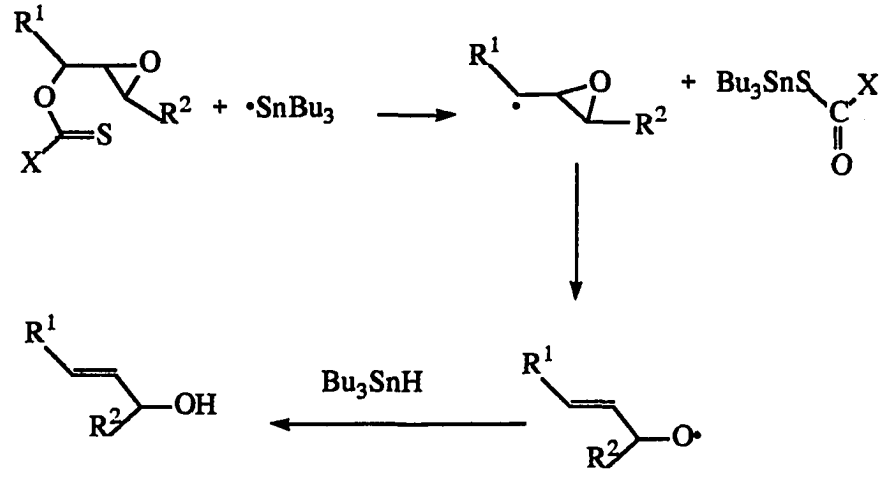
Scheme 5-3



Trialkylboranes react with oxygen or *tert*-butoxy radicals to generate alkyl radicals. In the presence of 1,3-butadiene monoxide, these alkyl radicals must add to the double bond of the epoxide to yield an intermediate radical 2, which then rearranges with the opening of the epoxide ring to 3. The alkoxyl radical 3 reacts with the trialkylborane to form the borinate 4, displacing an alkyl radical, which continues the chain. Hydrolysis of the intermediate borinate produces the 4-alkyl-2-buten-1-ol.

Barton et al.[23] have reported that the tri-*n*-butyltin hydride reduction of an α,β-epoxy-*O*-thiocarbonylimidazolide derivative leads via oxirane ring opening to the formation of an allylic alkoxyl radical as shown in Scheme 5-4.

Scheme 5-4

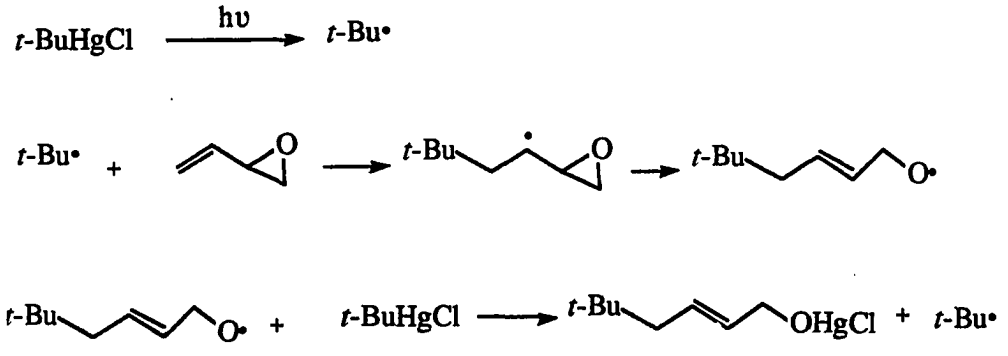


In this Part, we will examine the photostimulated reactions of vinylic epoxides with organomercury halides.

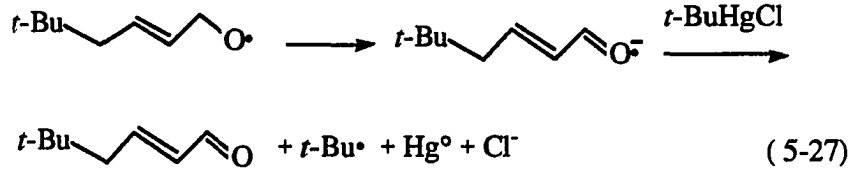
Results and Discussion

The reactions of 1,3-butadiene eopxide with organomercurials We expected butadiene monoxide to undergo a photostimulated reaction with *t*-BuHgCl to form the allyl alcohol via Scheme 5-5.

Scheme 5-5



In benzene the expected allyl alcohol and the alkoxymercury(II) salt were observed, but in a modest yield, possibly because the allyloxy radical does not readily displace *t*-Bu• from *t*-BuHgCl. In DMSO the yield of the allyl alcohol was very low, but significant amounts of the aldehyde (*E*-*t*-BuCH_2CH=CHCHO) were observed. This suggested that perhaps the allyloxy radical could lose a proton to form the ketyl radical anion which would readily transfer an electron to *t*-BuHgCl (Eq. 5-27)



(5-27)

Addition of DABCO (1,4-diazabicyclo[2.2.2]octane) as a proton acceptor had a siginificant effect upon the reaction in either benzene or DMSO solution. The allyl alcohol was no longer observed and *E*-*t*-BuCH_2CH=CHCHO and its alkylation product,

Table 5-1. Reactions of 1,3-butadiene epoxide and organomercurials in Rayonet photoreactor[a]

Mercurial (equiv)	Solvent	Conditions (equiv)
t-BuHgCl (5)	benzene	50h
t-BuHgCl (5)	benzene	9h, NH_4I (5)
t-BuHgCl (5)	benzene	5h, DABCO (3)
t-BuHgCl (5)	benzene	5h, NH_4I (5), DABCO (3)
t-BuHgI (5)	benzene	3h, NH_4I (5), DABCO (3)
t-BuHgCl (5)	DMSO	12h
t-BuHgCl (5)	DMSO	2h, NaI (5)
t-BuHgCl (5)	DMSO	8h, DABCO (5)
t-BuHgCl (5)	DMSO	1h, NaI (5), DABCO (3),
t-BuHgCl (5)	DMSO	3h, NaI (5), DABCO (3)
t-BuHgCl (5)	DMSO	1h, NaI (5), DABCO (3), $K_2S_2O_8$ (2)
t-BuHgCl (5)	DMSO	2h, NaI (5), DABCO (3), $K_2S_2O_8$ (2)

[a] The mixture in a 5 mm NMR tube was irradiated in Rayonet photoreactor.

% of R^1CHO[b]	% of R^2CHO[b]	% of R^3OH[b]	% of $R^3O(t\text{-Bu})$[b]	% of R^3OHgX[b]
0	0	39 (E isomer)	6	X = Cl,trace[c]
0	0	25 (E isomer)	8	X = I, trace[c]
37 (*E* / *Z* 28:9)	6	0	0	0
50 (*E* isomer)	13	0	0	0
53 (*E* isomer)	9	0	0	0
0	12	12 (*E* isomer)	0	0
5 (*E* isomer)	4	9 (*E* isomer)	0	0
17 (*E* isomer)	4	0	0	0
23 (*E* isomer)	0	0	0	0
14 (*E* isomer)	13	0	0	0
44[d](*E* isomer)	0	0	0	0
33[d](*E* isomer)	17[d]	0	0	0

[b] R^1 = *t*-$BuCH_2CH{=}CH$, R^2 = *t*-$BuCH_2CH(t\text{-Bu})CH_2$, R^3 = *t*-$BuCH_2CH{=}CHCH_2$, the yields were determined by ^1H NMR spectroscopy.

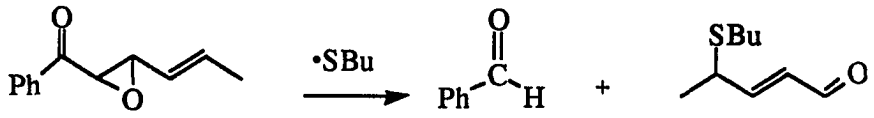
[c] *t*-$BuCH_2CH{=}CHCH_2OHgX$ was detected by GCMS.

[d] The yields were determined by GLC.

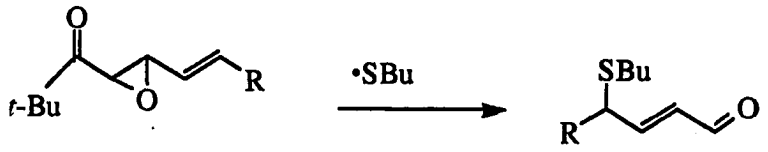
observed. When the organomercurial was changed from *t*-BuHgCl to *t*-BuHgI, the yields of the substituted allylic aldehyde were not significantly improved; 53% of *E*-*t*-$BuCH_2CH=CHCHO$ and 10% of *t*-$BuCH_2$(*t*-Bu)$CHCH_2CHO$ were obtained in 3 h.

When the solvent was changed from benzene to DMSO, the reactions of 1,3-butadiene epoxide with *t*-BuHgCl in DMSO under UV irradiation gave poor yields of the substituted allylic aldehyde (*E*-*t*-$BuCH_2CH=CHCHO$), alcohol (*E*-*t*-$BuCH_2CH=CHCH_2OH$), and disubstituted aldehyde (*t*-$BuCH_2$(*t*-Bu)$CHCH_2CHO$) but with very high regio- and stereoselectivity. The yields of the reactions of 1,3-butadiene epoxide with *t*-BuHgCl in DMSO under UV irradiation were not improved by the presence of I^-. The reaction carried out in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) under the same conditions gave only the aldehydes; with no alcohol was detected, but the yields of the reactions were poor. However, the reaction gave 44% of *E*-*t*-$BuCH_2CH=CHCHO$ as the only product in 1 h under UV irradiation in the presence of 5 equiv of NaI, 3 equiv of DABCO, and 2 equiv of $K_2S_2O_8$. The yield of *E*-*t*-$BuCH_2CH=CHCHO$ deceased to 33% and 17% of *t*-$BuCH_2$(*t*-Bu)$CHCH_2CHO$ was observed after 2 h under UV irradiation. The yields and products of these reactions are dependent upon the co-reactants and solvents.

From the literature review, nucleophilic 1,4-additions to 1,3-butadiene epoxides give the allylic alcohols as the final products and allylic aldehydes have never been reported. Murphy and co-workers[24] have reported that radical-induced cleavage of a ketoepoxide leads to the α,β-unsaturated aldehydes with yields between 19-29%.



(5-28)

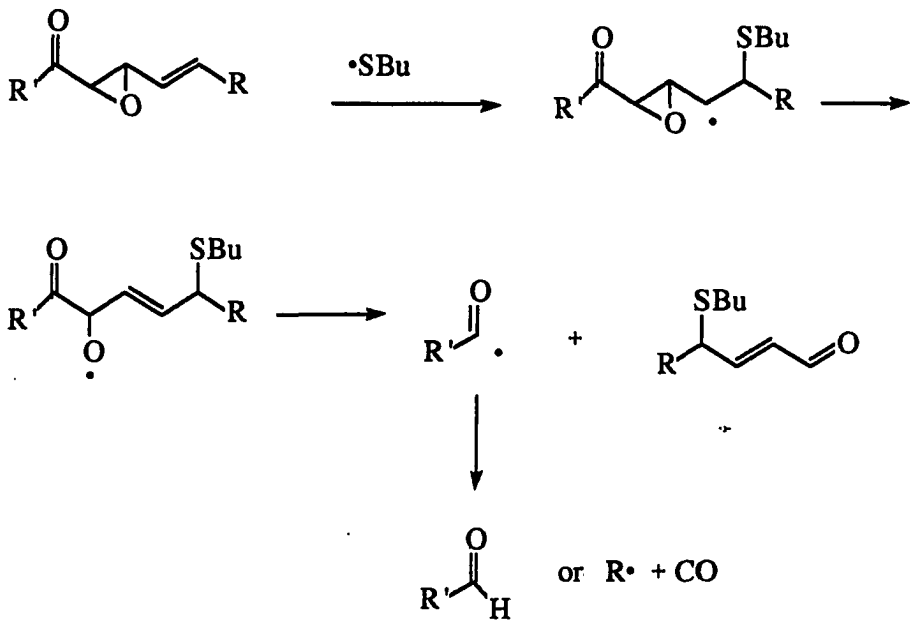


(5-29)

R = Me, H

The mechanism for these reactions was proposed as shown in Scheme 5-7. Thiyl radical addition to the epoxide is followed by epoxide C-O bond cleavage to yield the oxyradical which forms the α,β-unsaturated aldehydes and benzoyl radical. The benzoyl radical abstracts a hydrogen atom from the surrounding medium to yield the benzaldehyde, but for pivalyl radical (R = *t*-Bu), rapid decarbonylation ensues to give a *t*-Bu• which forms volatile products.

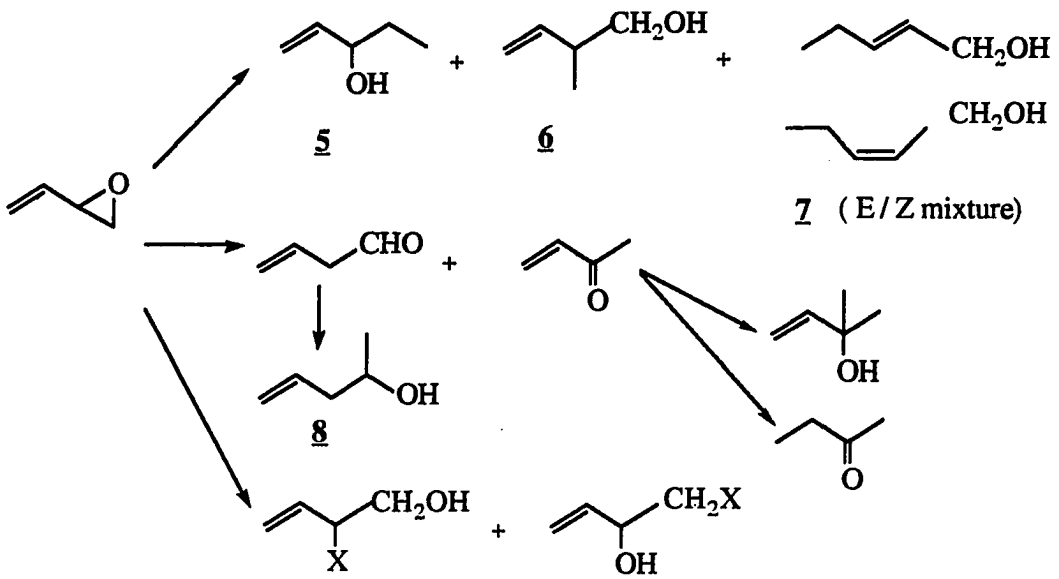
Scheme 5-7



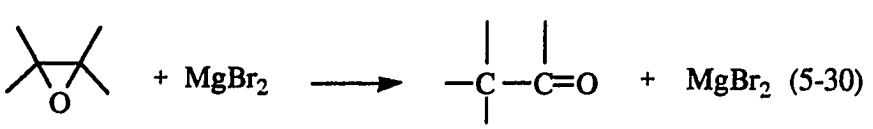
The reactions of 1,3-butadiene epoxide with organomercurials in benzene in the presence of DABCO gives the substituted allylic aldehyde as a major product. In the absence of DABCO, the reactions give the substituted allylic alcohol as the major product. When the reactions are carried out in DMSO, in the presence or absence of DABCO, the substituted allylic aldehyde is the major product. We find the formation of the substituted allylic aldehyde with 100% regio- and stereoselectivity to be surprising since the reactions of 1,3-butadiene epoxide with phenyl- and vinylmercury chloride in the presence of a stoichiometric amount of palladium(II) gave the substituted allylic alcohols with good yields (Eq. 5-25, 26).[21] Even in the presence of a base, vinylic epoxides react with alkyllithium reagents to give substituted allylic alcohols.[7]

Johsnson and Herr[25] have studied the reactions of 1,3-butadiene epoxide with a series of metallomethyl reagents. The various anticipated reaction paths are shown in Scheme 5-8.

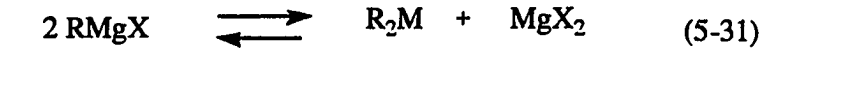
Scheme 5-8



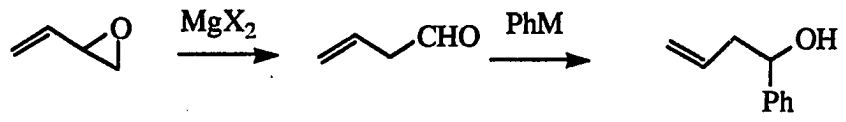
The compounds 5-8 were obtained in these reactions and the compound 7 was a major product in all reactions. House[26] reported that cis-trans 2,3-epoxybutane with magnesium bromide isomerized to 2-butanone.



Rose and Taylor[27] have reported that the reaction 1,3-butadiene epoxide with phenylmagnesium bromide in ether solution gave 73% of $H_2C{=}CHCH_2CH(OH)Ph$. They proposed the mechanism shown in the following equations.



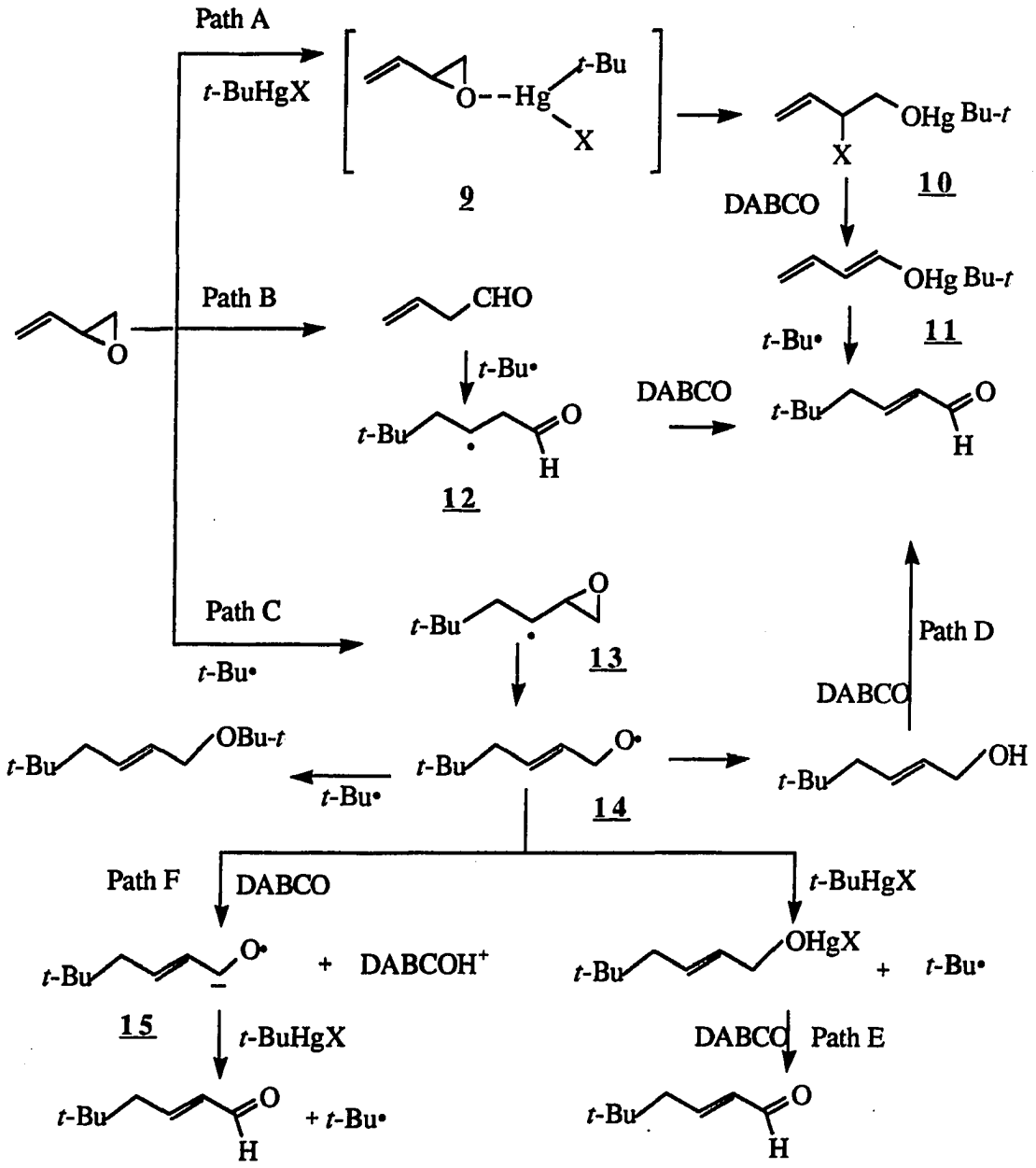
(5-31)



(5-32)

The possible pathways for the formation of *E-t*-$BuCH_2CH{=}CHCHO$ and *E-t*-$BuCH_2CH{=}CHCH_2OH$ from the reactions of 1,3-butadiene epoxide with organomercurials in the presence of co-reactants are shown in Scheme 5-9.

Scheme 5-9


Path A
t-BuHgX
t-Bu
O--Hg
X
9
OHg Bu-t
X
10
DABCO
OHg Bu-t
11
t-Bu•
Path B
CHO
t-Bu•
t-Bu
O
H
12
DABCO
t-Bu
O
H
Path C
t-Bu•
t-Bu
O
13
Path D
DABCO
OBu-t
t-Bu
t-Bu•
t-Bu
O•
14
OH
t-Bu
Path F
DABCO
t-BuHgX
O•
t-Bu
+ DABCOH+
15
OHgX
t-Bu
+ t-Bu•
t-BuHgX
DABCO
Path E
t-Bu
O
H
+ t-Bu•
t-Bu
O
H

The reaction of 1,3-butadiene epoxide with organomercurials might proceed via Path A. The intermediate **9**, formed from the reaction of 1,3-butadiene epoxide and *t*-BuHgX in DMSO solution, might rearrange to intermediate **10**. The intermediate **10** could react with DABCO in an E-2 type process to produce the intermediate **11**. The conjugate addition of *tert*-butyl radical to the intermediate **11** forms the *E*-*t*-$BuCH_2CH=CHCHO$.

The formation of *E*-*t*-$BuCH_2CH=CHCHO$ might be expected from Path B in Scheme 5-9. The 1,3-butadiene epoxide might rearrange to $H_2C=CHCH_2CHO$. Addition of *tert*-butyl radical to the $H_2C=CHCH_2CHO$ produces the intermediate radical **12** which might react with DABCO to form *E*-*t*-$BuCH_2CH=CHCHO$ via *t*-$BuCH_2CH=CHCHO^{-\bullet}$.

A third general process is the conjugation addition of *tert*-butyl radical to 1,3-butadiene epoxide to yield the intermediate radical **13** followed by cleavage of the C-O bond to form the oxyradical **14**. The oxyradical **14** might undergo the following steps to give the reaction products: (1) It might abstract a proton from the surrounding medium to form *E*-*t*-$BuCH_2CH=CHCH_2OH$, which somehow reacts with DABCO to form the substituted allylic aldehyde (Path D). (2) It might couple with *tert*-butyl radical to form the *E*-*t*-$BuCH_2CH=CHCH_2O$(*t*-Bu). (3) It might react with *t*-BuHgX to form the *E*-*t*-$BuCH_2CH=CHCH_2OHgX$ and *t*-Bu• which continues the chain; the *E*-*t*-$BuCH_2CH=CHCH_2OHgX$ with DABCO might give the substituted allylic aldehyde (Path E). (4) DABCO might accept the proton from the intermediate **14** to form intermediate anion radical **15** which undergoes electron transfer with *t*-BuHgX to form *E*-*t*-$BuCH_2CH=CHCHO$ and *t*-Bu• which continues the chain (Path F).

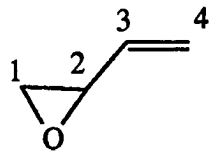
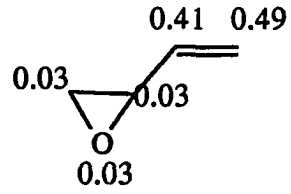
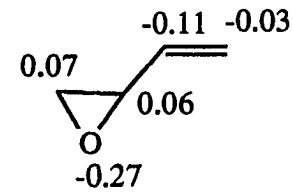
The intermediate **9** was observed by the NMR spectra analysis of the reaction of 1,3-butadiene epoxide with *t*-BuHgCl in DMSO in the dark, but was not observed in

benzene in the dark. The rate of formation of the intermediate **9** was catalyzed by $AgNO_3$ in DMSO under UV irradiation and 60-90% of the intermediate **9** was obtained in 1 h. The intermediate **9** in the presence or absence of DABCO with UV irradiation for 1 h gave none of the substituted allylic aldehyde and none of the intermediate **9** was recovered. This indicates that intermediate **9** is not responsible for the formation of the substituted allylic aldehyde from the reaction of 1,3-butadiene epoxide with *t*-BuHgCl in DMSO either in the presence or absence of DABCO under photolysis. However, the formation of intermediate **9**, which decomposes under UV irradiation, might be responsible for the low yield of *E*-*t*-$BuCH_2CH{=}CHCHO$ in these reactions.

The rearrangement of 1,3-butadiene epoxide to $H_2C{=}CHCH_2CHO$ did not occur in reactions, carried out in DMSO or benzene, of 1,3-butadiene epoxide with $HgCl_2$ in the presence of DABCO or Et_3N under UV irradiation in 24 h; more than 80% of 1,3-butadiene epoxide was recovered. Path A and B of Scheme 5-9 are thus excluded as the mechanism of the formation of the allylic aldehyde.

Font et al.[28] have reported that the behavior of conjugated oxiranes towards nucleophiles can be rationalized by means of pertubational theory and MNDO calculations. 1,3-Butadiene epoxide has been analyzed by MNDO. The results are shown in Table 5-2. 1,3-Butadiene epoxide shows no contribution of the C-1 and C-2 atomic orbitals in its LUMO and the largest coefficient is at the C-4 carbon atom. A soft nucleophile is most likely to react at this point leading to 1,4-addition with ring opening.

Table 5-2. 1,3-Butadiene Epoxide with LUMO and Atomic Charge Distribution obtained by MNDO

Experimental site of attack	LUMO	Charge distribution
		

The *t*-Bu• can easily attacks C-4 of 1,3-butadiene epoxide to form intermediate radical **13**, then, cleavage of C-O bond forms intermediate oxyradical **14** (Path C in Scheme 5-9). The reactions of 1,3-butadiene epoxide (0.1 M) and *t*-BuHgCl (0.5 M) without DABCO in benzene solution gave 39% of *E*-*t*-$BuCH_2CH{=}CHCH_2OH$, 6% of *E*-*t*-$BuCH_2CH{=}CHCH_2O(t\text{-Bu})$, and a trace of *t*-$BuCH_2CH{=}CHCH_2OHgCl$ in 50 h under UV irradiation. In the presence of NH_4I (0.5 M), the reaction gave 26% of *E*-*t*-$BuCH_2CH{=}CHCH_2OH$, 6% of *E*-*t*-$BuCH_2CH{=}CHCH_2O(t\text{-Bu})$, and a trace of *t*-$BuCH_2CH{=}CHCH_2OHgI$ in 4 h. From the product analysis, the intermediate radical **14** seems to be involved in these reactions. The intermediate radical **14** can abstract a proton to form *E*-*t*-$BuCH_2CH{=}CHCH_2OH$ which might be oxidized by the base to produce *E*-*t*-$BuCH_2CH{=}CHCHO$. However, the reaction of *t*-$BuCH_2CH{=}CHCH_2OH$ (*E* / *Z* 3.8 : 1) (0.1 M) with *t*-BuHgCl (0.5 M) in the presence of DABCO (0.3 M) and NH_4I (0.5 M) in DMSO or benzene under UV irradiation for 30 min, gave none of

t-$BuCH_2CH=CHCHO$ and 100% of the starting material was left. Even when the mixture was photolyzed for 24 h, more than 90% of *t*-$BuCH_2CH=CHCH_2OH$ was recovered and no aldehyde was detected. This suggests that Path D of Scheme 5-9 does not occur.

E-*t*-$BuCH_2CH=CHCH_2O$(*t*-Bu) was apparently formed by the coupling of *t*-Bu• with intermediate **14**. With 0.2 equiv of 1,3-butadiene epoxide and 1 equiv of *t*-BuHgCl, the ratio of *E*-*t*-$BuCH_2CH=CHCH_2OH$ to *E*-*t*-$BuCH_2CH=CHCH_2O$(*t*-Bu) is 4.3 : 1, but with 0.5 equiv of 1,3-butadiene epoxide and 1 equiv of *t*-BuHgCl, the ratio increases to 39 : 1.

A trace amount of *E*-*t*-$BuCH_2CH=CHCH_2OHgX$ (X = I or Cl) was detected by GCMS in the reaction of 1,3-butadiene epoxide (0.1 M) and *t*-BuHgCl (0.5 M) in benzene solution with NH_4I (0.5 M) under UV irradiation for 9 h or without NH_4I for 50 h. When 3 equiv of DABCO was added to the solution and the mixture photolyzed for another 3 h, no *t*-$BuCH_2CH=CHCHO$ was detected. This indicates that Path E of Scheme 5-9 does not occur.

We believe Path F of Scheme 5-9 is the only possible rational explanation for the formation of *t*-$BuCH_2CH=CHCHO$ in the reaction, in benzene solution of 1,3-butadiene epoxide and *t*-BuHgCl in the presence of DABCO under UV irradiation. An electron transfer between the intermediate anion radical **15** and *t*-BuHgX gives the substituted allylic aldehyde and *t*-Bu• which continues the chain reaction. The kinetic chain length of the reaction of 1,3-butadiene epoxide and *t*-BuHgI in the presence of NH_4I and DABCO was measured as 126 (see page 140).

The reaction of 1,3-butadiene epoxide , NaI, and *t*-BuHgCl in the absence of DABCO in DMSO solution under UV irradiation gave the substituted aldehydes and alcohol as major products, but in poor yields. Possibly DMSO can accept a proton from

intermediate radical **14** to form intermediate **15** which produces the *t*-$BuCH_2CH$=CHCHO.

Addition of the *tert*-butyl radical to *t*-$BuCH_2CH$=CHCHO forms the disubstituted aldehyde, *t*-$BuCH_2$(*t*-Bu)$CHCH_2CHO$. This was proved by the reaction of *t*-$BuCH_2CH$=CHCHO ($E/Z = 4.8$) (0. 1 M) with *t*-BuHgCl (0.5 M) in the presence of I^- in DMSO solution under UV irradiation to give *t*-$BuCH_2$(*t*-Bu)$CHCH_2CHO$ in 27 % yield.

Determination of the kinetic chain length of the reaction between 1,3-butadiene epoxide and *tert*-butylmercury iodide The reaction of 1,3-butadiene epoxide and organomercurials has been shown to be a radical process since the reactions fail to occur in the dark and when irradiated the reactions are inhibited by the presence of di-*tert*-butyl nitroxide. However, the kinetic chain lengths of these reactions are not known. In order to provide evidence to support the chain process of these reactions, it is necessary to measure the kinetic chain lengths for these reactions.

An initial kinetic chain length for the radical reaction can be formulated as shown in equation 2-1 (page 57). Both the initial rate and rate of initiation can be measured experimentally by following either the rate of consumption of the substrate or rate of formation of the substitution product. The progress of the reaction is conveniently monitored by ^1H NMR spectroscopy.

1,3-Butadiene epoxide, *t*-BuHgI, DABCO, NH_4I in a nitrogen-purged deuterated benzene were placed in an NMR tube. The solution was irradiated at 350 nm and was checked at different periods of time by ^1H NMR spectroscopy. The formation of products was determined by following the increase of NMR spectra signals for the

protons from the aldehydes and the new double bond which appears at 9.34, 9.92 ,6.34 , and 5.84 ppm. Yields of the products were obtained from integration of appropriate ^1H NMR signals relative to an internal standard and the results are listed in Table 5-3. The plot of yields of the substituted aldehydes vs. time is shown in Fig. 5-1 (curve A).

Table 5-4 includes the results from the reaction in the presence of di-*tert*-butyl nitroxide (DTBN) which was carried out under the same conditions as the reaction without DTBN. The plot of yields of the substituted aldehydes vs. time is shown in Figure. 5-1 (curve B).

The initial rate of the reaction is obtained from the initial slope of the curve as shown in Figure 5-1 and calculated as 5.52×10^{-2} M/min. The time, for which the reaction was inhibited by 1.67×10^{-2} M DTBN, is 38 min (Figure 5-1). The rate of initiation with inhibitor (DTBN) presents is obtained from the concentration of DTBN divided by the time needed to consume all of the DTBN which can be determined from Figure 5-1. The reaction of 1,3-butadiene epoxide and *t*-BuHgI in the presence of DABCO and NH_4I is definitely a radical chain process with an initial kinetic chain length of 126.

From Figure 5-1

Initial Rate = 5.52×10^{-2} (M / min)

Rate of Initiation = $1.67 \times 10^{-2} / 38$ (M / min)

Kinetic Chain Length = 125.6

Table 5-3. Reaction of 1,3-butadiene epoxide and *t*-BuHgI in benzene-d_6 in the presence of NH_4I and DABCO[a,b]

Time	% *t*-BuCH_2CH=CHCHO	% *t*-BuCH_2CH(*t*-Bu)CHCHO	Total %Yield[c]
0	0	0	0
120	42	6	48
180	53	9	62
240	49	12	61
300	41	15	56

[a] The reaction of 1,3-butadiene epoxide (0.1 M), *t*-BuHgI (0.5 M), NH_4I (0.5 M), and DABCO (0.3 M) without DTBN were carried out in benzene-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated in a Rayonet photoreactor.

[c] Determined by the ^1H NMR spectroscopy; benzene was used as an internal standard.

Table 5-4. Reaction of 1,3-butadiene epoxide and *t*-BuHgI in benzene-d_6 in the presence of NH_4I, DABCO and DTBN[a,b]

Time	% *t*-BuCH_2CH=CHCHO	% *t*-BuCH_2CH(*t*-Bu)CHCHO	Total % Yield[c]
0	0	0	0
10	0	0	0
20	0	0	0
30	0	0	0
90	19	0	19
198	41	8	49
243	49	11	60
543	50	15	65

[a] The reaction of 1,3-butadiene epoxide (0.1 M), *t*-BuHgI (0.5 M), NH_4I (0.5 M), and DABCO (0.3 M) with DTBN (0.0167 M) were carried out in benzene-d_6.

[b] The mixture in a 5 mm NMR tube was irradiated in a Rayonet photoreactor.

[c] Determined by the ^1H NMR spectroscopy; benzene was used as an internal standard.

Curve A : without DTBN

Curve B: with DTBN, 1.67×10^{-2} M

Initial Rate = (5.52×10^{-1}) x 0.1 M = 5.52×10^{-2} M / min

Inhibited time = 38 min

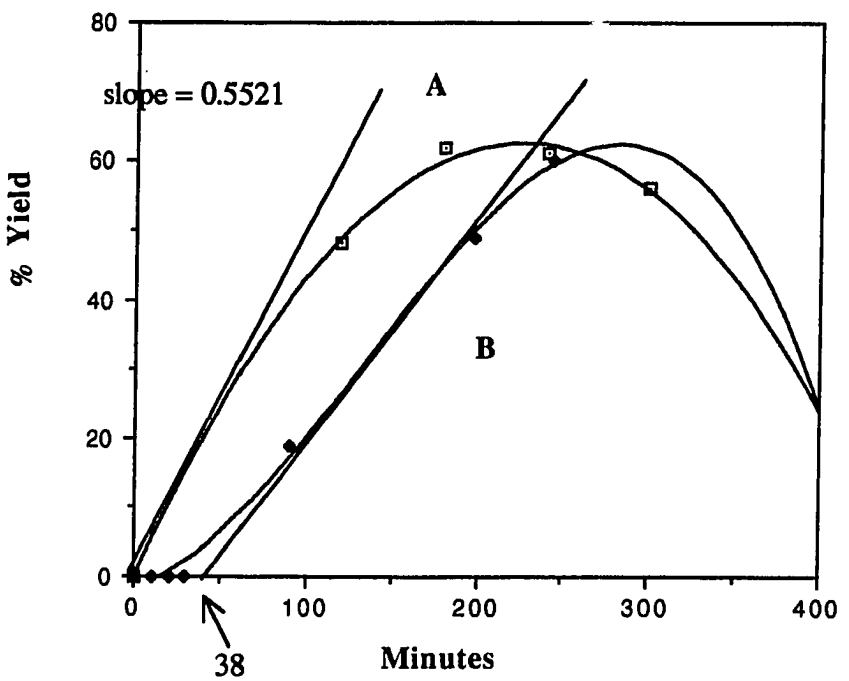
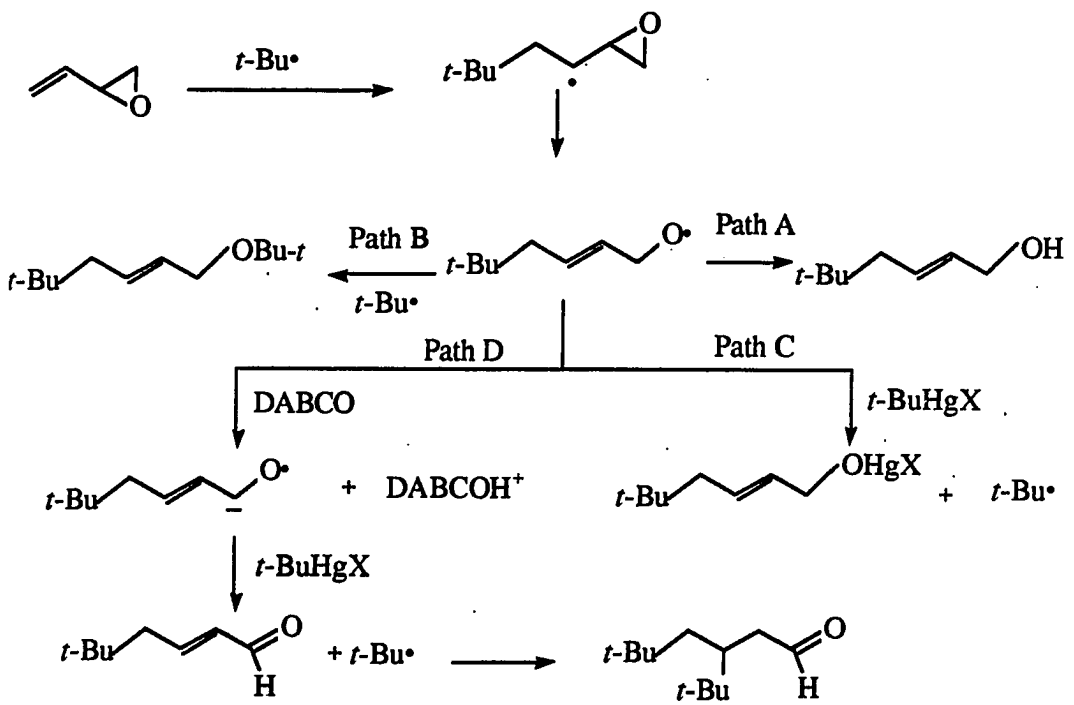


Figure 5-1. Formation of products vs. time for the reaction of 1,3-butadiene epoxide and *tert*-butylmercury iodide

Mechanistic consideration The reactions of 1,3-butadiene epoxide and organomercurials in the presence of DABCO and I^- presented in this part are believed to involve free radical reactions. This is based on the finding that the reactions only proceeded when irradiated, are inhibited by the presence of di-*tert*-butyl nitroxide, and the kinetic chain length was measured to be 126. The mechanism is believed to involve the addition of *tert*-butyl radical to 1,3-butadiene epoxide in benzene solution as outlined in Scheme 5-10.

Scheme 5-10

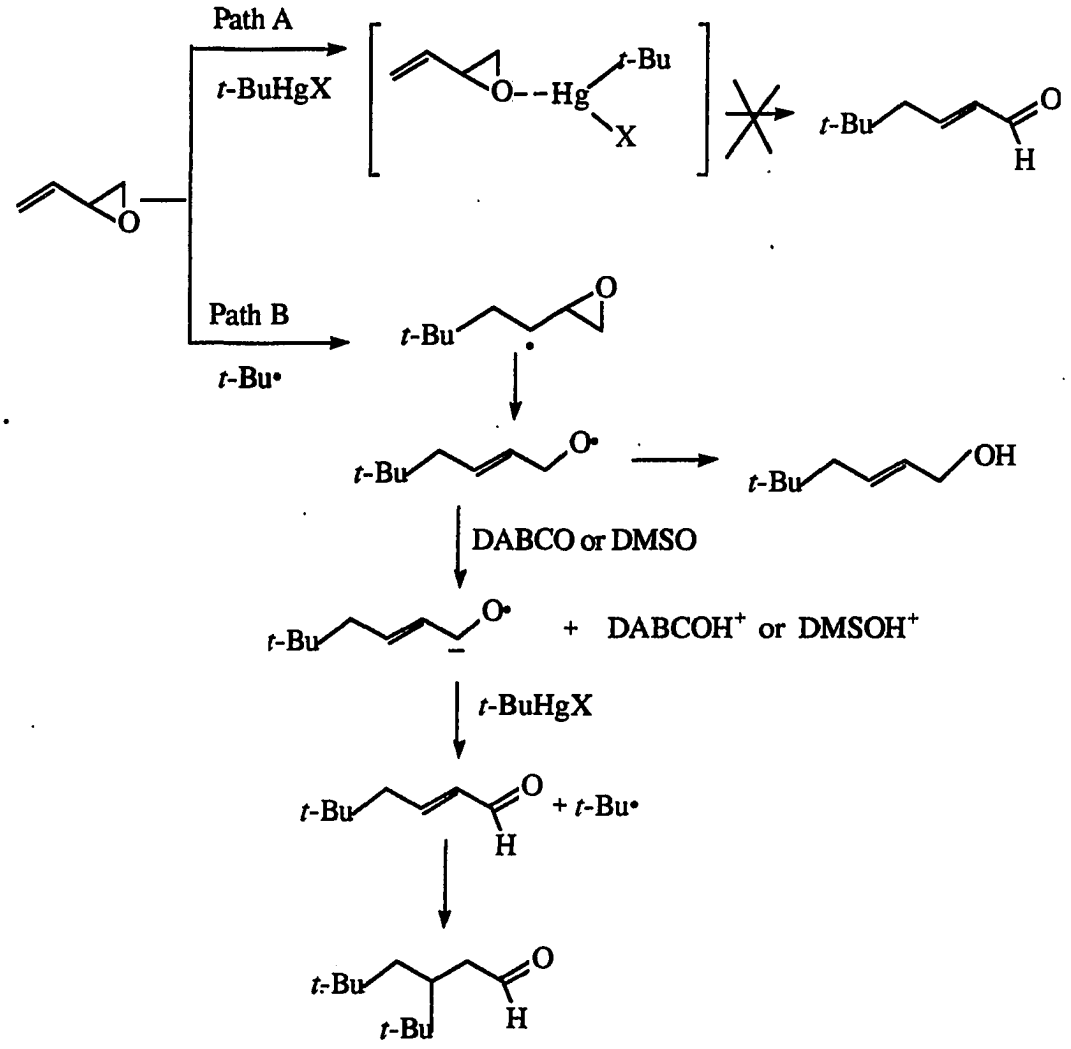


The reactions, which were carried out in benzene in the absence of DABCO, follow the Paths A, B, and C in Scheme 5-10 to give *E*-*t*-BuCH_2CH=CHCH_2OH,

E-*t*-$BuCH_2CH$=$CHCH_2O$(*t*-Bu), and a trace of *t*-$BuCH_2CH$=$CHCH_2OHgX$. Path A is the dominant pathway in the reactions without DABCO, while in the presence of DABCO, the reaction proceeds by Path D to give *E*-*t*-$BuCH_2CH$=CHCHO which reacts further with *tert*-butyl radical to yield *t*-$BuCH_2$(*t*-Bu)$CHCH_2CHO$.

The mechanism of the reaction in DMSO solution of 1,3-butadiene epoxide and organomercurials in the presence of co-reactants is shown in Scheme 5-11. In DMSO solution, the oxygen of 1,3-butadiene epoxide can coordinate with the mercury atom of *t*-BuHgX to form the ate complex, which decomposes under photolysis and might lead to the substituted aldehyde in low yield (Path A in Scheme 5-11). However, the experimental results cited previously argue against this route. The reaction in DMSO without DABCO still gave *E*-*t*-$BuCH_2CH$=CHCHO. This indicates that the DMSO can serve as a base to accept a proton from the oxyradical (Path B in Scheme 5-11). However, the reaction is much more efficient in the presence of an added base such as DABCO.

Scheme 5-11



Conclusion

The photostimulated reactions of 1,3-butadiene epoxide with organomercurials give the substituted aldehydes, alcohol and ether with very high regio- and stereoselectivity. The yields and products of the reactions are dependent upon the solvent and co-reactants.

In benzene solution, the reactions in the presence of DABCO give the *E*-isomer of the substituted allylic aldehyde as the major product. Minor amounts of the disubstituted aldehyde are formed. The reactions without DABCO in benzene give the *E*-isomer of the substituted allylic alcohol as the major product. Minor amounts of the *E*-isomer of the substituted allylic ether and a trace of allyloxymercury halide are also formed. In DMSO solution, the reactions give modest yields of substituted aldehydes in the presence of DABCO, while without DABCO, the reactions give substituted aldehydes and alcohol as products in poor yields.

The reactions are believed to occur via a free-radical addition to the vinyloxiranes. The preferred mechanisms are shown in Schemes 5-10 and 5-11. DABCO or DMSO can accept a proton from the oxyradical intermediate in these reactions.

Experimental Section

General considerations ^{1}H NMR spectra were recorded on a Nicolet Magnetic Corp. NMC-1280 spectrometer (300 MHz) in DMSO-d_6 or benzene-d_6. Product yields were determined by ^{1}H NMR integration with a known amount of biphenyl or benzene as an internal standard. Gas chromatographic analysis was performed on a 3700 Varian gas chromatograph with a packed Chromosorb W (80-100 mesh) column coated with 7% OV-3 and a thermal conductivity detector. Product yields were determined by addition of a known amount of biphenyl or toluene as an internal standard.

tert-Butylmercury chloride and iodide were prepared as previously described (see Part I). 1,3-Butadiene epoxide and DABCO were purchased from Aldrich Chemical

Company and used without further purification. Solvents were purchased and dried as mentioned before.

Preparation of *t*-BuCH$_2$CH=CHCH$_2$OH A solution of copper(I) iodide (20 mmol) and dry ether (100 ml) under nitrogen was cooled to -78 °C at which temperature 1.7 M *tert*-butyllithium in pentane solution (40 mmol) was added dropwise over 10 min. The solution was stirred at -78 °C for 60 min, before the 1,3-butadiene epoxide (20 mmol) was added dropwise into the solution at -78 °C over a period of 5 min. The solution was stirred for another 60 min at -78 °C. Saturated aqueous ammonium chloride (20 ml) was added at 0 °C. After the mixture was stirred at 0 °C for 10 min, it was extracted twice with ether. The ether layer was washed with water several times and dried over anhydrous sodium sulfate. The ether was removed by vacuum and the products was purified by distillation. The alcohols were analyzed by ^{1}H NMR spectroscopy and found to have an *E*/*Z* on ratio of 3 : 1 and bp 45-46 °C at 1 mm Hg.

E-isomer of *t*-BuCH$_2$CH=CHCH$_2$OH: ^{1}H NMR ($CDCl_3$) δ 5.71 (m , 2 H), 4.13 (d, J = 5.1 Hz, 2 H), 1.96 (d, J = 6.9 Hz, 2 H), 0.90 (s, 9 H); GCMS *m* / *z* (relative intensity) 128 (M^+, 1.97), 110 (5), 95 (20), 82 (4), 69 (14), 57 (100), 41 (66).

Z-isomer of *t*-BuCH$_2$CH=CHCH$_2$OH: ^{1}H NMR ($CDCl_3$) δ 5.71 (m , 2 H), 4.21 (d, J = 6.1 Hz, 2 H), 1.99 (d, J = 7.2 Hz, 2 H), 0.92 (s, 9 H).

Preparation of *t*-BuCH$_2$CH=CHCHO A sufficient quantity of a 5 % of dipyridine chromium(VI) oxide[29] in anhydrous dichloromethane was prepared to provide a sixfold molar ratio of complex to alcohol. This excess was usually required for complete oxidation to the aldehyde. The freshly prepared, pure complex dissolved completely in dichloromethane at 25 °C at 5 % concentration to give a red deep solution. The *t*-BuCH$_2$CH=CHCH$_2$OH(E / Z = 3) was added to the red solution in one

portion with stirring at 0 °C for 3 h. The supernatant liquid was decanted from the precipitate and the precipitate was rinsed thoroughly with dichloromethane.

The combined dichloromethane solution was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water to remove excess trace of pyridine and chromium salts. The products were obtained by evaporation of dichloromethane and purified by distillation. The products are analyzed by ^{1}H NMR spectroscopy as having an *E* / *Z* ratio of 4.8 : 1, bp 56-58 °C at 12 torr (lit.[30] bp 56-58 °C at 12 torr).

E-isomer of *t*-BuCH_2CH=CHCHO: ^{1}H NMR ($CDCl_3$) δ 9.54 (d, *J* = 8.1 Hz, 1 H), 6.93 (ddt , *J* = 15.6, 7.8, 1.2 Hz, 1 H), 6.15 (dd, *J* = 15.6, 7.8 Hz, 1 H), 2.24 (dd, *J* = 7.8, 1.2 Hz, 2 H), 0.97 (s, 9 H); GCMS *m* / *z* (relative intensity) 127 (M+ 1^+, 0.2), 111 (3), 95 (3 0), 83 (6), 70 (100), 57 (96), 55 (28), 41 (64), 39 (23). GCMS (CI, NH_3) *m* / *z* (relative intensity) 161 ($(M + 35)^+$, 5), 144 ($(M + 18)^+$, 100). GCIR (relative intensity) 2966 (50), 2734 (16), 1715 (100), 1636 (20), 1167 (16), 1105 (26), 976 (16), 887 (15), 650 (21) cm^{-1}.

Z-isomer of *t*-BuCH_2CH=CHCHO: ^{1}H NMR ($CDCl_3$) δ 10.08 (d, *J* = 8.1 Hz, 1 H), 6.73 (dt , *J* = 11.4, 7.2 Hz, 1 H), 6.15 (overlaps with E isomer, 1 H), 2.52 (d, *J* = 7.2 Hz, 2 H), 0.99 (s, 9 H).

Photostimulated reactions of 1,3-butadiene epoxide with organomercurials 1,3-Butadiene epoxide (0.1 M) and co-reactants (see Table 5-1 for equivalents) were dissolved in the deoxygenated solvent under a nitrogen atmosphere in a Pyrex test tube equipped with a rubber septum. The mixture was irradiated in a Rayonet photoreactor at 350 nm for the period time indicated in the Table 5-1. After irradiation, a known amount of the internal standard biphenyl was dissolved in the reaction mixture. The reaction mixture was then poured into a saturated aqueous

sodium chloride solution and extracted with diethyl ether. The extracted ether was washed twice with 20% sodium thiosulfate solution to remove any unreacted organomercury halide, dried over anhydrous sodium sulfate, and carefully concentrated under vacuum. The mixture was then analyzed by GC and GCMS.

Reactions of 1,3-butadiene epoxide with *tert*-butylmercury halides were conveniently performed in an NMR tube and monitored by ^{1}H NMR spectroscopy. Thus, 0.1 mmol of the substrate and the co-reactant (see Table 5-1 for equivalents) were dissolved in 1 ml DMSO-d_6 or benzene-d_6 in an NMR tube closed with a cap and sealed with teflon tape. The ^{1}H NMR spectroscopy was recorded before irradiation with benzene or dichloromethane as an internal standard. The mixture was photolyzed in a Rayonet photoreactor and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. The yield of product was obtained from integration of the appropriate peaks in the reaction product. Yields of the substitution products are summarized in Table 5-1.

The identification of the substitution products, in many cases, was confirmed by comparison of their ^{1}H NMR spectroscopy and GCMS data with those of the authentic compounds synthesized by known literature methods or by comparison of their ^{1}H NMR spectroscopy data with those of the compounds reported in the literature. The following products were obtained from the reactions reported in Table 5-1.

E-*t*-BuCH_2CH=CHCH_2OH and *E*-*t*-BuCH_2CH=CHCHO were identified by comparing GC retention time, GCMS, and ^{1}H NMR spectroscopy with the authentic compounds.

E-*t*-BuCH_2CH(*t*-Bu)CH_2CHO : ^{1}H NMR ($CDCl_3$) δ 9.79 (dd, J = 2.7, 1.2 Hz, 1 H), 2.71 (ddd, J = 18.3, 8.4, 2.7 Hz, 1 H), 2.27 (ddd, J = 18.3, 5.4, 1.2 Hz, 1

H), 1.94 (m, 3 H), 0.90 (s, 9 H), 0.80 (s, 9 H); GCMC *m / z* (relative intensity) 185 (M + 1 $^{+}$, 0.09), 169 (0.29), 128 (15), 95 (11), 81 (5), 69 (11), 57 (100), 41 (29). GCIR (relative intensity) 2964 (100), 2883 (40), 2814 (24), 2708 (28), 1738 (52), 1485 (31), 1396 (24), 1371 (30), 1221 (22), 1209 (22).

t-$BuCH_2CH=CHCH_2OHgX$ was detected by GCMS only, because it decomposed after workup with $Na_2S_2O_3$ or water. From the GCMS, the structures of these compounds seem reasonable.

t-$BuCH_2CH=CHCH_2OHgCl$: GCMS *m / z* (relative intensity) 366 (0.01), 204-198 (0.1), 179 (4), 126 (12), 11 (3), 110 (8), 109 (12), 95 (7), 83 (9), 69 (5), 57 (100), 41 (12).

t-$BuCH_2CH=CHCH_2OHgI$: GCMS *m / z* (relative intensity) 456-452 (0.1), 388-382 (0.3), 373-367 (0.1), 331-325 (1), 204-198 (2), 169 (0.4), 128 (0.6), 127 (1.2), 110 (0.5), 95 (0.5), 57 (100), 41 (43), 39 (10).

t-$BuCH_2CH=CHCH_2O$(*t*-Bu): ^{1}H NMR (C_6D_6) δ 5.65−5.54 (m, 2 H), 3.84 (dd, *J* = 3.9, 0.9 Hz, 2 H), 1.91 (d, *J* = 6.9 Hz, 2 H), 0.865 (s, 9 H); GCMS *m / z* (relative intensity) 184 (M^+, 0.09), 181 (0.11), 169 (0.06), 128 (17), 111 (5), 95 (12), 81 (4), 69 (9), 59 (13), 57 (100), 56 (13), 55 (18).

The formation of [1,3-butadiene epoxide----*t*-BuHgCl] complex

1,3-Butadiene epoxide (0.1 mmol), *t*-BuHgCl (0.5 mmol), and DABCO (0.3 mmol) were dissolved in 1 ml DMSO-d_6 in an NMR tube wrapped with aluminum foil and closed with a cap sealed with teflon tape. The ^{1}H NMR spectroscopy was recorded before irradiation with benzene or dichloromethane as an internal standard. The mixture was heated in a Rayonet photoreactor and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. The complex was observed by ^{1}H NMR

spectroscopy; a 70% yield of the complex was formed after 30 h. The complex could not be isolated because it decomposed after workup with sodium thiosulfate or water. The rate of formation of this complex from the reaction of 1,3-butadiene epoxide and *t*-BuHgCl was catalyzed by the presence of $AgNO_3$. 1,3-Butadiene epoxide (0.1 mmol), *t*-BuHgCl (0.5 mmol), and $AgNO_3$ (0.2 mmol) were dissolved in 1 ml DMSO-d_6 in an NMR tube closed with a cap sealed with teflon tape. The ^1H NMR spectroscopy was recorded before irradiation with benzene or dichloromethane as an internal standard. The mixture was irradiated in the Rayonet photoreactor and the progress of the reaction was monitored periodically by ^1H NMR spectroscopy. The yield of the complex was 60-90 % in 1 h.

After more than 70 % of the complex had been formed from the reaction in the dark or in the reaction catalyzed by $AgNO_3$, the mixture was irradiated in the Rayonet photoreactor for several hours to give only a trace of the substituted aldehydes.

[1,3-butadiene epoxide----*t*-BuHgCl] complex: ^1H NMR (DMSO-d_6) δ 5.87 (ddd, J = 17.4, 10.8, 6.6 Hz, 1 H), 5.53 (d, J = 17.4 Hz, 1 H), 5.43 (d, J = 10.8 Hz, 1 H), 4.98 (m, 1 H), 3.75 (dd, J = 12.6, 3 Hz, 1 H), 3.52 (dd, J = 12.6, 8.7 Hz, 1 H), 1,39 (s, 9 H); GCMS *m / z* (relative intensity) 366-360 (~ 0.5), 320-312 (~7), 276 (16), 275 (2), 274 (62), 273 (21), 272 (100), 271 (54), 270 (66), 269 (38), 268 (24), 239 (3), 238 (0.7), 237 (6), 236 (3), 235 (4), 234 (2), 204 (14), 202 (58), 201 (26), 200 (47), 199 (34), 198 (21), 136 (9), 135 (11), 101 (7), 99 (7), 66 (12), 57 (3).

The reaction of 1,3-butadiene epoxide with $HgCl_2$ in the presence of DABCO or Et_3N 1,3-Butadiene epoxide (0.1 mmol), $HgCl_2$ (0.5 mmol), and DABCO (or Et_3N) (0.3 mmol) were dissolved in 1 ml of DMSO-d_6 in an NMR tube closed with a cap sealed with teflon tape. The ^1H NMR spectroscopy was

recorded before irradiation with benzene or dichloromethane as an internal standard. The mixture was photolyzed in a Rayonet photoreactor and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. More than 80 % of the epoxide was recovered after 24 h and no H_2C=$CHCH_2CHO$ was detected.

The reaction of *t*-$BuCH_2CH$=$CHCH_2OH$ with *t*-BuHgCl in the presence of DABCO and NH_4I *t*-$BuCH_2CH$=$CHCH_2OH$ (0.1 mmol, *E* / *Z* = 3), *t*-BuHgCl (0.5 mmol), NH_4I (0.5 mmol), and DABCO (0.3 mmol) were dissolved in 1 ml DMSO-d_6 or benzene-d_6 in an NMR tube closed with a cap and sealed with teflon tape. The ^{1}H NMR spectroscopy was recorded before irradiation with benzene or dichloromethane as an internal standard. The mixture was photolyzed in a Rayonet photoreactor and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. More than 90 % of the alcohol was recovered after 24 h and no *t*-$BuCH_2HC$=$CHCHO$ was detected.

The reaction of *t*-$BuCH_2HC$=$CHCHO$ with *t*-BuHgCl in the presence of NH_4I *t*-$BuCH_2CH$=$CHCHO$ (0.1 mmol, *E* / *Z* = 4.8), *t*-BuHgCl (0.5 mmol), and NH_4I (0.5 mmol) were dissolved in 1 ml DMSO-d_6 in an NMR tube closed with a cap and sealed with teflon tape. The ^{1}H NMR spectroscopy was recorded before irradiation with benzene or dichloromethane as an internal standard. The mixture was photolyzed in a Rayonet photoreactor and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. The yield of product was obtained from the integration of the appropriate peaks in the reaction product. the compound *t*-$BuCH_2CH$(*t*-Bu)CH_2CHO (27%) was obtained in 3.5 h.

Determination of the initial kinetic chain length of the reaction of 1,3-butadiene epoxide with *tert*-butylmercury iodide 1,3-Butadiene epoxide (0.5 mmol), *t*-BuHgI (2.5 mmol), NH_4I (2.5 mmol) and benzene (0.5 mmol) were dissolved in 5 ml of nitrogen-purged deuterated benzene. The solution was divided into ten NMR tubes (0.5 ml in each tube) each equipped with a rubber septum. After a 300 MHz ^1H NMR spectrum was obtained, the NMR tubes were irradiated in a Rayonet photoreactor. Tubes were removed after a period of time and the yield of the substitution product obtained from tintegration of the proton signals of the aldehydes. The yields of the substitution products at different periods of time are presented in Table 5-3.

The reaction of 1,3-butadiene epoxide with *t*-BuHgI and NH_4I in the presence of DTBN was also carried out under the same conditions. The concentration of DTBN was 1.67×10^{-2} M. After a 300 MHz ^1H NMR spectrum had been obtained, the NMR tubes were irradiated in the Rayonet photoreactor. Tubes were removed after a period of time and the yield of substitution products obtained from integration of the proton signals of the aldehydes. The yields of the substitution products at different periods of time are presented in Table 5-4.

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