

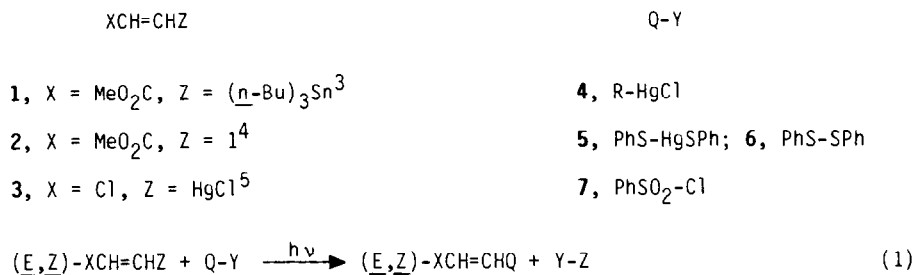
STEREOSPECIFIC VINYL SUBSTITUTIONS OCCURRING
 BY FREE RADICAL ADDITION-ELIMINATION

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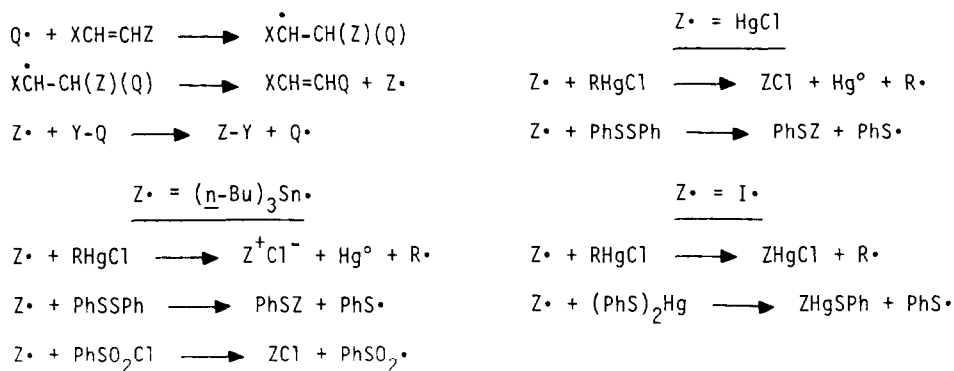
Summary: The free radical chain reaction between cyclohexyl-HgCl and (E) or (Z) MeO₂CCH=CHSnBu₃, MeO₂CCH=CHI, or ClCH=CHHgCl forms MeO₂CCH=CHC₆H₁₁ or ClCH=CHC₆H₁₁ in a stereospecific manner with retention of stereochemistry.

We have found that vinylic free radical substitution proceeding by an addition-elimination mechanism can proceed in a stereospecific manner although the selectivity in forming (Z)-1,2-disubstituted alkenes from a (Z)-precursor is sometimes low. The (E)- and (Z)-isomers of 1-3 have been studied in Reaction 1 proceeding according to the chain reaction of Scheme 1.^{1,2} Results listed in Table 1 were obtained from starting materials with the following isomeric purities: (Z)-1, 98% (GLPC); (E)-1, 98% (GLPC); (Z)-2, 97% (GLPC); (E)-2, >99% (GLPC); (Z)-3, 75% (¹H NMR); (E)-3, >98% (¹H NMR).

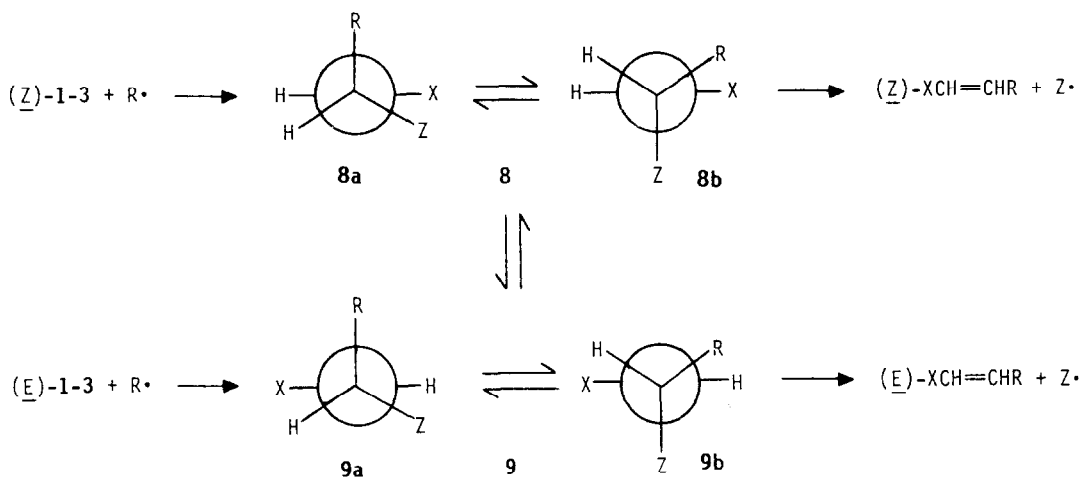


It is clear from Table 1 that the reactions of 1-3 with Q* = cyclo-C₆H₁₁* are stereospecific and that a higher specificity is observed for Z = I than for Z = (n-Bu)₃Sn. Isomerization of 1-3 as well as isomerization of the resulting vinyl sulfides under the reaction conditions (sunlamp or 350 nm irradiation in PhH or Me₂S₂O) was a contributing factor to the stereoselectivities observed, particularly with the (Z)-reactants. Reaction of (E) and (Z)-2 with cyclo-C₆H₁₁HgCl for 0.5 h with sunlamp irradiation yielded substitution products with (E)/(Z) = 33 and 0.2 while recovered starting material had (E)/(Z) = 39 and 0.1, respectively.

Scheme 1



The elimination of $Z\cdot$ (Scheme 1) is apparently faster for $Z = \text{I}$ or HgCl than for $Z = \text{Bu}_3\text{Sn}$. Thus, with $Q = \text{Me}_3\text{C}\cdot$ or $\text{PhS}\cdot$, stereospecificity was not observed with **1** but was observed with **2** and **3**. Elimination of $Z = \text{I}$, HgCl or SnBu_3 with $Q = 2^\circ\text{-alkyl}$ must be faster than the equilibrium between **8** and **9**. With $R = \text{Me}_3\text{C}$ the $\text{8} \rightleftharpoons \text{9}$ interconversion was slower than the β -elimination of $Z = \text{I}$ or HgCl , but with $Z = \text{Bu}_3\text{Sn}$ only (E)- $\underline{t}\text{-BuCH}=\text{CHCO}_2\text{Me}$ was observed. Reaction of (E) or (Z)-**1** with $\text{PhSO}_2\cdot$ (from PhSO_2Cl) also gave only the



(E)-product. With a bulky R group ($\underline{t}\text{-Bu}$, PhSO_2) and with $Z = \text{Bu}_3\text{Sn}$ and $X = \text{MeO}_2\text{C}$, conformation **8b** is apparently bypassed because of steric considerations and elimination only occurs from the more stable **9b**.

Table 1. $XCH=CHZ + QY \xrightarrow{h\nu} XCH=CHQ + YZ$

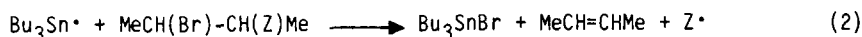
Reactant	QY(equiv.)	Conditions ^a	Product (%)
(E)-1	cyclo-C ₆ H ₁₁ HgCl (5)	PhH, SL, 2 h	20, $\underline{E/Z}$ = 36 ^b
(Z)-1	cyclo-C ₆ H ₁₁ HgCl (5)	PhH, SL, 2 h	34, $\underline{E/Z}$ = 2.5 ^c
(E)-1	cyclo-C ₆ H ₁₁ HgCl (1.5)	PhH/Me ₂ SO, UV, 5 h	66, $\underline{E/Z}$ = 23
(Z)-1	cyclo-C ₆ H ₁₁ HgCl (1.5)	PhH/Me ₂ SO, UV, 5 h	70, $\underline{E/Z}$ = 2.1
(E)-1	Me ₃ CHgCl (1.6)	PhH, UV, 5 h	36, $\underline{E/Z}$ > 50
(Z)-1	Me ₃ CHgCl (1.6)	PhH, UV, 5 h	49, $\underline{E/Z}$ > 50
(E)-2	<i>i</i> -PrHgCl (1.6)	PhH, SL, 4 h	36, $\underline{E/Z}$ = 30
(Z)-2	<i>i</i> -PrHgCl (1.6)	PhH, SL, 6 h	35, $\underline{E/Z}$ = 0.5
(Z)-2	<i>i</i> -PrHgCl (1.6)	PhH, UV, 23 h	45, $\underline{E/Z}$ = 0.5
(E)-2	cyclo-C ₆ H ₁₁ HgCl (5)	PhH/Me ₂ SO, SL, 0.5 h	$\underline{E/Z}$ = 33
(Z)-2	cyclo-C ₆ H ₁₁ HgCl (5)	PhH/Me ₂ SO, SL, 0.5 h	$\underline{E/Z}$ = 0.2
(E)-2	cyclo-C ₆ H ₁₁ HgCl (5)	PhH/Me ₂ SO, SL, 6 h	34, $\underline{E/Z}$ = 20
(Z)-2	cyclo-C ₆ H ₁₁ HgCl (5)	PhH/Me ₂ SO, SL, 6 h	45, $\underline{E/Z}$ = 0.9
(E)-2	Me ₃ CHgCl (5)	PhH, SL, 6 h	43, $\underline{E/Z}$ > 50
(Z)-2	Me ₃ CHgCl (5)	PhH, SL, 6 h	41, $\underline{E/Z}$ = 0.1
(E)-3	cyclo-C ₆ H ₁₁ HgCl (1.2)	Me ₂ SO, UV, 10 h	28, $\underline{E/Z}$ = 4.3
(Z)-3 ^d	cyclo-C ₆ H ₁₁ HgCl (1.2)	Me ₂ SO, UV, 10 h	39, $\underline{E/Z}$ = 0.7
(E)-3	Me ₃ CHgCl (1.2)	Me ₂ SO, UV, 10 h	33, $\underline{E/Z}$ = 5.6
(Z)-3 ^d	Me ₃ CHgCl (1.2)	Me ₂ SO, UV, 10 h	44, $\underline{E/Z}$ = 2.7
(E)-1	PhSSPh (1.6)	PhH, UV, 8 h	79, $\underline{E/Z}$ = 3.8 (8 h) 8.9 (5 min)
(Z)-1	PhSSPh (1.6)	PhH, UV, 8 h	91, $\underline{E/Z}$ = 3.7
(E)-1	PhSO ₂ Cl (1.6)	PhH, UV, 10 h	68, $\underline{E/Z}$ > 50
(Z)-1	PhSO ₂ Cl (1.6)	PhH, UV, 10 h	76, $\underline{E/Z}$ > 50
(E)-2	Hg(SPh) ₂ (1.6)	PhH/Me ₂ SO, SL, 1 h	19, $\underline{E/Z}$ = 4.8 ^e
(E)-2	Hg(SPh) ₂ (1.6)	PhH/Me ₂ SO, UV, 6 h	60, $\underline{E/Z}$ = 3.5
(Z)-2	Hg(SPh) ₂ (1.6)	PhH/Me ₂ SO, SL, 1 h	10, $\underline{E/Z}$ = 1.9 ^f
(Z)-2	Hg(SPh) ₂ (1.6)	PhH/Me ₂ SO, UV, 6 h	69, $\underline{E/Z}$ = 3.6
(E)-3	PhSSPh (1.2)	Me ₂ SO, SL, 0.5 h	X = Cl; 14, $\underline{E/Z}$ = 3.4 X = SPh; 56, $\underline{E/Z}$ = 0.9
(E)-3	PhSSPh (0.5)	Me ₂ SO, UV, 6 h	X = Cl; 20, $\underline{E/Z}$ = 2.5 X = SPh; 40, $\underline{E/Z}$ = 0.6
(Z)-3 ^d	PhSSPh (0.5)	Me ₂ SO, UV, 6 h	X = Cl; 16, $\underline{E/Z}$ = 0.9 X = SPh; 32, $\underline{E/Z}$ = 0.7
(E)-3	PhSSPh (1.2)	Me ₂ SO, UV, 6 h	X = SPh; 81, $\underline{E/Z}$ = 0.7
(Z)-3 ^d	PhSSPh (1.2)	Me ₂ SO, UV, 6 h	X = SPh; 81, $\underline{E/Z}$ = 0.8

(Z)-C ₂ H ₂ Cl ₂	cyclo-C ₆ H ₁₁ HgCl (0.5)	Me ₂ SO, UV, 20 h ⁹	70, $\underline{E/Z} = 0.8$
(Z)-C ₂ H ₂ Cl ₂	cyclo-C ₆ H ₁₁ HgCl (1.0)	Me ₂ SO, UV, 20 h ⁹	45, $\underline{E/Z} = 0.7$
(Z)-C ₂ H ₂ Cl ₂	Me ₃ CHgCl (1.0)	Me ₂ SO, UV, 20 h ⁹	42, $\underline{E/Z} > 50$
(Z)-C ₂ H ₂ Cl ₂	(PhS) ₂ Hg (0.2)	Me ₂ SO, UV, 20 h ⁹	X = Cl; 5, $\underline{E/Z} = 0.4$ X = PhS; 81, $\underline{E/Z} = 0.5$
(E)-C ₂ H ₂ Cl ₂	cyclo-C ₆ H ₁₁ HgCl (0.5)	Me ₂ SO, UV, 20 h ⁹	63, $\underline{E/Z} = 0.7$
(E)-C ₂ H ₂ Cl ₂	Me ₃ CHgCl (0.3)	Me ₂ SO, UV, 20 h ⁹	75, $\underline{E/Z} > 50$
(E)-C ₂ H ₂ Cl ₂	(PhS) ₂ Hg (0.2)	Me ₂ SO, UV, 20 h ⁹	X = Cl; 14, $\underline{E/Z} = 0.4$ X = PhS; 84, $\underline{E/Z} = 0.5$

^a1 mmol of substrate in 10 mL of solvent was irradiated under N₂ in a Pyrex tube; SL = 275 W sunlamp ca. 20 cm from reaction flask; UV = 350 nm Rayonet reactor. ^bRecovered 1 (75%) had $\underline{E/Z} = 10$. ^cRecovered 1 (47%) had $\underline{E/Z} = 0.1$. ^dStarting material had $\underline{Z/E} = 3.0$. ^eRecovered 2 had $\underline{E/Z} = 66$. ^fRecovered 2 had $\underline{E/Z} = 0.2$. ^g2-5 mmol of C₂H₂Cl₂ in 5 mL Me₂SO.

Reaction of 3 with PhSSPh demonstrated that chlorine can also serve as a leaving group in Scheme 1. Reaction of (E) or (Z)-1,2-dichloroethylene with (PhS)₂Hg with photostimulation yielded a mixture of (E) and (Z)-PhSCH=CHSPh with no stereospecificity ($\underline{E/Z} = 0.5$). Alkyl-mercurials also underwent a photostimulated reaction with ClCH=CHCl but with replacement of only one of the chlorine atoms. The lack of stereospecificity observed for free radical substitutions in C₂H₂Cl₂ is consistent with Cl[•] being a poorer leaving group than I[•], HgCl or Bu₃Sn[•]. PhSCH=CHCl is obviously much more reactive than C₂H₂Cl₂ towards PhS[•] and should be a good substrate for other substitution reactions proceeding by Scheme 1.

Stereospecificity has been previously reported in Reaction 2 with Z = Br⁶ or SO₂Ph⁷ but not with Z = SPh or SO₂Ph.⁸



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