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THE NONCUMULATIVE EFFECT OF METHYL SUBSTITUENTS ON THE RATE OF ADDITION OF BENZENESELENENYL CHLORIDE TO OLEFINS[1]

GEORGE H. SCHMID* and DENNIS G. GARRATT[2]
Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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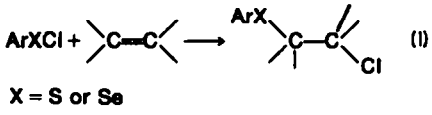
Abstract—The rates and products of addition of benzeneselenenyl chloride to ethylene and its six Me substituted derivatives have been determined in methylene chloride at 25°. Unlike the addition of 4-chlorobenzenesulfenyl chloride to this same series of compounds, the effect of Me groups on the rates of addition is not cumulative. Also the regiochemistry of the product is different. For arenesulfenyl chloride additions, products of *anti*-Markownikoff orientation are formed preferentially under conditions of kinetic control. Under similar conditions regiospecific formation of the Markownikoff adduct is observed for the addition of benzeneselenenyl chloride to methylpropene and 2-methyl-2-butene. These data indicate a difference in both rate and product determining transition states between additions of arenesulfenyl and selenenyl chlorides to alkenes.

Since sulfur and selenium belong to the same group of the periodic table, it is not surprising that reactions of structurally identical sulfur and selenium compounds should be similar. For example arenesulfenyl and areneselenenyl chlorides both add to alkenes to form β-chloroalkyl aryl sulfides and selenides respectively (eqn 1).



(1)

X = S or Se

In both cases the adducts are formed by stereospecific *anti*-addition and the rate law is overall second order; first order in both alkene and sulfenyl or selenenyl chloride.[3]

From the data available, it is not clear if this similarity extends to the mechanisms of the two reactions. We would like to present data which clearly show that arenesulfenyl and areneselenenyl chlorides exhibit different structure-reactivity profiles in the reactions with ethylene and its methyl substitutied derivatives and discuss the mechanistic implications of this fact.

RESULTS

Kinetics. We have measured the rate of addition of benzeneselenenyl chloride to ethylene 1 and all its methyl substituted derivatives 2–7 in anhydrous methylene chloride at 25° by means of the stopped-flow technique using a Durrum–Gibson stopped-flow spectrophotometer. The rate of disappearance of benzeneselenenyl chloride was followed by measuring the decrease in its absorption at 433 nm. The addition was found to exhibit second order kinetics, first order in alkene, and first order in selenenyl chloride to at least 80% completion of the reaction. The rate data were calculated using the standard second order integrated rate expression. These data are compiled in Table 1.

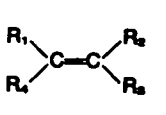
Table 1. Second order rate constants for the addition of benzeneselenenyl chloride to a series of methyl substituted ethylenes in methylene chloride at 25°C

Compound	No. of methyl groups	$k_2(M^{-1}s^{-1})$	k_{rel}
Ethylene (1)	0	498	1.0
Propene (2)	1	4360	8.8
Z-2-Butene (3)	2	1870	3.8
E-2-Butene (4)	2	1040	2.1
Methylpropene (5)	2	3370	6.8
2-Methyl-2-butene (6)	3	1880	3.8
2,3-Dimethyl-2-butene (7)	4	1230	2.5

Products. The stereo- and regiochemistry of the adducts was determined by ^1H and ^{13}C NMR spectroscopy, The isolation and characterization of the products of the addition of benzeneselenenyl chloride to ethylene, propene and methylpropene have previously been described and hence will not be considered in detail here.[4]

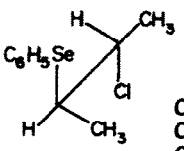
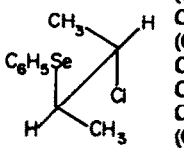
The ^1H NMR spectrum of the adduct derived from Z-2-butene shows a doublet of quartets at δ3.58 and δ4.23 ppm with a vicinal proton–proton coupling constant of 3.2 Hz in chloroform-d. In contrast the ^1H NMR spectrum of the adduct derived from E-2-butene shows asymmetric "quintets" in its 60 MHz spectrum with a vicinal coupling constant of 6.7 Hz.

The relative configurations of the two adducts were assigned by observing the variation in $^3J_{H,H}$ with solvent dielectric constant (see Table 2).[5] For the *threo* ((*RS*) (*RS*)) compound $^3J_{H,H}$ should increase with increasing solvent dielectric whereas for the *erythro* ((*RS*)(*SR*)) compound a decrease should be observed. Further $^3J_{H,H}$ (*threo*) is generally less than $^3J_{H,H}$ (*erythro*). Thus we have assigned the product from Z-2-butene as 2 - (*RS*), 3 - (*RS*) - 3 - chlorobutyl - 2 phenyl



	R_1	R_2	R_3	R_4		R_1	R_2	R_3	R_4
1:	H	H	H	H					
2:	CH_3	H	H	H	5:	CH_3	H	H	CH_3
3:	CH_3	CH_3	H	H	6:	CH_3	CH_3	CH_3	H
4:	CH_3	H	CH_3	H	7:	CH_3	CH_3	CH_3	CH_3

Table 2. Solvent dependence of vicinal proton–proton coupling constants for (2-*RS*, 3-*RS*) and (2-*RS*, 3-*SR*)-3-chlorobutyl-2 phenyl selenide

Compound	Solvent	Dielectric constant	J_{AB}(Hz)
 2-*RS*, 3-*RS*	CCl_4	2.23	2.5
	$CDCl_3$	4.70	3.2
	CD_3CO_2D	6.19	3.4
	$(CD_3)_2C{=}O$	20.7	3.6
	CD_3NO_2	38.6	3.8
	$(CD_3)_2S{=}O$	49.0	3.8
 2-*RS*, 3-*SR*	CCl_4	2.23	6.8
	$CDCl_3$	4.70	6.7
	CD_3CO_2D	6.19	6.4
	$(CD_3)_2C{=}O$	20.7	6.2
	CD_3NO_2	38.6	6.0
	$(CD_3)_2S{=}O$	49.0	5.8

selenide and that from E-2-butene as 2 - (*RS*), 3 - (*SR*) - 3 - chlorobutyl - 2 phenyl selenide.

The reaction of benzeneselenenyl chloride with 2 - methyl - 2 - butane gave a single adduct, **8** which was assigned the Markownikoff regiochemistry on the basis of the similarities of the relative proton chemical shifts compared to those of the analogous sulfur containing compound.[6] The assignment was confirmed by the ^{13}C NMR spectrum of **8** which has a doublet at δ53.39 ppm with a ^{77}Se–^{13}C coupling constant of 47.5 Hz.

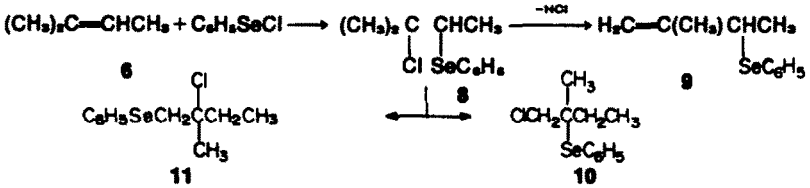
conclude that the addition of benzeneselenenyl chloride occurs in an *anti*-stereospecific manner.

DISCUSSION

The mechanism of the electrophilic addition of arenesulfenyl chlorides to alkenes is known to involve a bridged rate-determining transition state. Among the data that lead to this conclusion is the observation of a cumulative effect on the rate caused by substituting Me groups for hydrogen on ethylene.[6] Similar results have been obtained for bromination,[7] chlorination[8] and epoxidation of alkenes.[9] The mechanisms of all these reactions involve a bridged rate-determining transition state.

Because of the similarities of the additions of arenesulfenyl and areneselenenyl chlorides to alkenes, it might be expected that a similar cumulative effect would be observed in the selenium analogs. It is clear from the data in Table 1 that this expectation is not realized. Furthermore the effect of methyl groups on the rate is much less in the case of the selenium electrophile; only 9 fold compared to 120 fold for 4-chlorobenzenesulfenyl chloride. This small rate increase is due to a decrease in the rates when two or more methyl groups are bonded to the double bond. Such a reactivity pattern is inconsistent with an open carbonium-ion-like rate-determining transition state.[10] In electrophilic additions such substituent effects are usually attributed to steric hindrance between the electrophile and the substituents around the double bond.[11] Thus it appears that the addition of benzeneselenenyl chloride is more susceptible to steric hindrance that the analogous sulfur electrophile.

Our data provide evidence for a difference in the rate-determining transition states for addition of the two



Compound **8** readily undergoes further reaction. It eliminates HCl to form **9** and rearranges to form **10** and **11** in about equivalent amounts.

The formation of **10** and **11** from **8** has no precedent in the sulfur analogs. Compounds **10** and **11** are not formed by isomerization of **6** to 2-methyl-1-butene **12** followed by addition of benzeneselenenyl chloride. The addition of benzeneselenenyl chloride to **12** under the same conditions yields only the Markownikoff adduct **11**. Furthermore, **11** isomerizes to **10** very slowly taking several weeks to reach equilibrium. In contrast the formation of **10** and **11** from **8** takes only a few days.

The reaction of benzeneselenenyl chloride with 2,3 - dimethyl - 2 - butene, **7**, gave as the first formed product 3 - chloro - 2,3 - dimethylbutyl - 2 phenyl selenide. Its identity is based on the similarity of the two singlets at δ1.83 and δ1.51 ppm in the ^1H NMR spectrum integrating at six protons each, with those of the analogous sulfide.[6] It is thermally unstable; further decomposition and rearrangements were apparent from the change in the ^1H NMR spectrum with time. Details of these reactions will be reported at a later date.

Based upon the ^1H and ^{13}C NMR data we can

electrophiles. This difference may be due to entirely different transition state structures which differ in geometry and/or charge distribution. Alternatively it may be due to a difference only in the degree of bond making in transition states of similar structures. Thus bond making would be more advanced in the transition state for the addition of benzeneselenenyl chloride relative to that for the addition of the sulfenyl chloride. It is impossible to distinguish between these two alternatives from our data.

There is also a difference in the product determining steps. The regiochemistry of the products of addition of benzeneselenenyl and 4-chlorobenzenesulfenyl chlorides to methylpropene and 2-methyl-2-butene differ greatly as illustrated in Table 3. While the difference in regiochemistry for the additions to propene (**2**) is small, the regiospecific formation of Markownikoff products under conditions of kinetic control is opposite to that normally found for additions of arenesulfenyl chlorides to **5** and **6**. This fact has been explained by the preferred attack of chloride ion at the least hindered carbon of the thiiranium ion intermediate.[12] An explanation for the observed products of additional of benzeneselenenyl

chloride involving an open carbonium ion after the rate-determining transition state for geminal disubstituted alkenes seems incorrect in view of the known regio- and stereospecific addition of 2,4-dinitrobenzeneselenenyl chloride to *cis*- and *trans*-1-phenylpropene.[13]

It has been reported recently that ion-pairs are important in the product determining steps of additions of arenesulfenyl chlorides to alkenes.[14] It may be that products are formed from different ion-pairs in the two additions. Thus products of sulfenyl chloride additions may result from intimate or solvent-separated ion-pairs while the products of benzeneselenenyl chloride may be formed from dissociated ions. Support for this view comes from the reactions of stable thiiranium ions.[12] These ions, which are believed to resemble dissociated ions, react with external chloride ion to form exclusively products of Markownikoff orientation.

In summary, our data show a difference in the additions of arenesulfenyl and selenenyl chlorides to alkenes. It is not clear if this is due to entirely different mechanisms for the two reactions or small differences within the same general mechanism.

Table 3. The kinetically controlled product composition of additional of benzeneselenenyl chloride and 4-chlorobenzenesulfenyl chloride to 2, 5 and 6

Alkene	Addition of C_6H_5SeCl[a]		Addition of 4-ClC_6H_4SCl[b]	
	M[c]	aM[c]	M[c]	aM[c]
$CH_3CH{=}CH_2$ (2)	59	41	62	38
$(CH_3)_2C{=}CH_2$ (5)	100	—	12	88
$(CH_3)_2C{=}CHCH_3$ (6)	100	—	35	65

[a]In CH_2Cl_2 at 25°. [b]In CCl_2HCHCl_2 at 25°. [c]M = Markownikoff orientation; aM = anti-Markownikoff orientation.

EXPERIMENTAL

The alkenes were obtained commercially and their purity and identity were verified by GLC and NMR.

Benzeneselenol was prepared by the Grignard method of Foster,[15] b.p. 39–40°/2 mm (lit. 57–58°/8 mm, 84–86°/25 mm).

Diphenyl diselenide was prepared from benzeneselenol by air oxidation. m.p. 62.5–63° (lit. m.p. 63°[16]) CMR $CDCl_3$: 131.44, 129.00, 127.54, 136.86.

Benzeneselenenyl chloride was prepared by the chlorination of diphenyl diselenide using one mole equivalent of sulfuryl chloride in CCl_4 at room temp. The product was isolated in 94% yield after removal of solvent and distillation, b.p. 95–96°/6 mm (lit. 92°/5 mm[16]). Upon standing the liquid solidified. Recrystallization from CH_2Cl_2, m.p. 63.7–64.5° (lit 64°[16]). UV λ_{max} 433 nm ϵ 264 l mole^{-1} cm^{-1}.

Purification of solvent, kinetics, product composition and analytical samples were carried out as previously described.[17]

Analytical and spectral data of products

(i) *From ethylene.* PMR $CDCl_3$ 100 MHz resolved as two multiplets of 12 lines each centered at δ 3.57 and 3.13 ppm analysis A_2B_2 spin system; CMR $CDCl_3$ δ43.11 $\underline{C}H_2Cl$ δ 43.11 $\underline{C}H_2Cl$ J_{SeCC} = 7.7 Hz, δ 28.96 $\underline{C}H_2Se$ J_{SeC} = 65.8 Hz.

(ii) *From propene.* Markownikoff adduct; PMR $CDCl_3$ $ABMX_3$ spin system, δ 4.10 ddq (1H) J = 9.7, 4.3, 6.3; 3.02 q (1 H), J = 12.5, 9.7; δ3.36 q (1 H), J = 12.4, 4.3 Hz; δ1.58 d(3 H) ^3J = 6.3 Hz; CMR $CDCl_3$ δ37.29 t $\underline{C}H_2Se$, J_{SeC} = 63.2 Hz, δ56.76 d $\underline{C}HCl$, δ24.35 q $\underline{C}H_3CHCl$; MS, *m/e* M^+ 234 M–Cl^+ 199, M–HCl^+ 198, M–$C_2H_4Cl^+$ 171. *anti*-Markownikoff adduct; PMR $CDCl_3$ $ABCX_3$ spin system, δ3.33–3.90 m (3 H), 1.49 d (3 H) ^3J = 6.5 Hz; CMR $CDCl_3$ δ18.64 q $\underline{C}H_3CHSe$, 39.07 d $\underline{C}HSe$ J_{SeC} = 62.7 Hz, 50.03 t $\underline{C}H_2Cl$ J_{SeCC} = 6.9 Hz; MS *m/e* M^+ 234, M–Cl^+ 199, M–HCl^+ 198, M–CH_2Cl^+ 185. Kinetic product distribution M:aM 59:41. Thermodynamic product distribution M:aM 100:0.

(iii) *From methylpropene.* A single product, 2-chloro-2-methyl propyl-1 phenyl selenide; PMR $CDCl_3$. δ 1.68 s (6 H), 3.41 s (2 H) $^2J_{SeH}$ = 11.2 Hz; CMR $CDCl_3$ δ44.79 t $\underline{C}H_2Se$ $^1J_{SeC}$ = 66.6 Hz, δ69.93 s $\underline{C}(CH_3)_2Cl$, $^2J_{SeC}$ = 7.9 Hz, δ31.85 q $(\underline{C}H_3)_2CCl$ $^3J_{SeC}$ = 15.5 Hz; MS *m/e* M^+ 248, M–Cl^+ 213, M–HCl^+ 212, M–$C_3H_6Cl^+$ 171.

Independent synthesis of the *anti*-Markownikoff adduct was accomplished by treating methylpropene in anhyd CH_2Cl_2 with phenylselenium trichloride,[16] and reduction of the corresponding selenide dichloride with $NaHSO_3$ aq[18] followed by extraction with pentane, PMR $CDCl_3$ δ1.41 s (6 H), 3.92 s (2 H) $^3J_{SeH}$ = 5.3 Hz CMR $CDCl_3$ δ28.06 q $(\underline{C}H_3)_2CSe$, J_{SeCC} = 8.1 Hz, δ54.96 s $\underline{C}(CH_3)_2Se$ J_{SeC} 63.1 Hz, δ52.03 t $\underline{C}H_2Cl$ J_{SeCC} = 7.8 Hz.

(iv) *From Z-2-butene.* PMR $CDCl_3$ δ1.48 d (3 H) J = 7.0 Hz, $\underline{C}H_3CHSe$, 3.58 dq (1 H) J = 7.0, 3.5 Hz, $\underline{C}HSe$, 4.23 dq (1 H) J = 6.9, 3.5 Hz, $\underline{C}HCl$, 1.56 d (3 H) J = 6.9 $\underline{C}H_3CHCl$; CMR $CDCl_3$ δ15.82 q $\underline{C}H_3CHSe$ $^2J_{SeCC}$ = 7.9 Hz, 45.89 d $\underline{C}HSe$ J_{SeC} = 62.5 Hz, 61.12 d $\underline{C}HCl$ J_{SeCC} = 7.3 Hz, 19.82 q $\underline{C}H_3CHCl$. (Found: C, 48.36; H, 5.03; Cl, 14.38. Calc. for $C_{10}H_{13}SeCl$: C, 48.50; H, 5.29; Cl, 14.31%).

(v) *From E-2-butene.* PMR $CDCl_3$ δ1.45 d (3 H) J = 7.0 Hz $\underline{C}H_3CHSe$, 3.32 q' (1 H) J = 7.0, 6.9 $\underline{C}HSe$, 4.15 q' (1 H) J = 6.8, 6.9 $\underline{C}HCl$, 1.51 d (3 H) J = 6.8 $\underline{C}H_3CHCl$; CMR $CDCl_3$ δ18.69 q $\underline{C}H_3CHSe$ J_{SeCC} = 10.1 Hz, 46.44 d $\underline{C}HSe$ J_{SeC} = 63.9 Hz, 62.88 d $\underline{C}HCl$ J_{SeCC} = 10.8 Hz, 24.16 q $\underline{C}H_3CHCl$ J_{SeCCC} = 16 Hz. (Found: C, 48.52; H, 5.23; Cl, 14.42. Calc. for $C_{10}H_{13}SeCl$: C, 48.50; H, 5.29; Cl, 14.31%).

(vi) *From 2-methyl-2-butene.* Compound **8**, PMR $CDCl_3$ δ 1.74 s (6 H) 1.63 d (3 H) J = 6.8, 3.49 q (1 H) J = 6.8; CMR $CDCl_3$ δ19.48 q $\underline{C}H_3CHSe$ J_{SeCC} = 6.5, 53.39 d $\underline{C}HSe$ J_{SeC} = 47.5, 74.51 s $\underline{C}(CH_3)_2Cl$, 29.34 q $\underline{C}H_3C(CH_3)Cl$, 32.73 q $\underline{C}H_3C(CH_3)Cl$. Compound **11**, PMR $CDCl_3$ δ3.67 s (2 H) J_{SeH} = 10.0 Hz, $\underline{C}H_2Se$, 1.60 s (3 H), 0.95 t (3 H) J = 8.0, 1.90 q (2 H) J = 8.0 Hz; CMR $CDCl_3$ δ 42.63 t $\underline{C}H_2Se$, 74.31 s $\underline{C}Cl$, 29.53 q $\underline{C}H_3CCl$, 35.77 t $\underline{C}H_2CCl$, 9.14 $\underline{C}H_3CH_2CCl$. Compound **10**, PMR $CDCl_3$ δ 1.00 t (3 H) J = 6.5, 1.8 q (2 H) J = 6.5, 1.58 s (3 H), 4.03 s (2 H) $\underline{C}H_2Cl$; CMR $CDCl_3$ δ50.33 t $\underline{C}H_2Cl$; 43.64 s $\underline{C}Se$, 29.98 q $\underline{C}H_3CSe$, 31.08 t $\underline{C}H_2CSe$, 9.13 q $\underline{C}H_3CH_2CSe$. Compound **9**, PMR $CDCl_3$ δ1.65 d (3 H) J = 6.7, 1.76 s (3 H), 3.52 q (1 H) J = 6.7, 5.13 M (2 H).

(vii) *From 2,3-dimethyl-2-butene.* 3 - Chloro - 2,3 - dimethyl - butyl - 2 - phenyl selenide, PMR $CDCl_3$ δ1.83 s (6 H), 1.51 s (6 H), $t_{1/2}$ CH_2Cl_2 ≈ 2–5 min. 30°.

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