Mechanistic Studies on the Addition Reactions of Benzeneselenenyl Bromide to Substituted Styrenes[1a]

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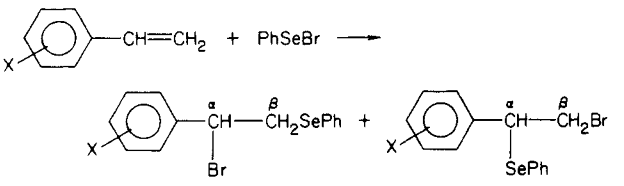
Second-order kinetics of the addition of benzeneselenenyl bromide to seven substituted styrenes was studied. The ρ and ρ^+ values were −0.37 and −0.27, respectively. The mechanisms were discussed and the product distributions were found to be strongly solvent dependent. ^{1}H, ^{13}C, as well as ^{77}Se NMR spectra were employed for product identification. The correlation between ^{77}Se NMR shifts for the adducts 1 and 2 and σ values were presented.

The use of organoselenium compounds in organic synthesis is well documented.[2] The mechanism for the addition of areneselenenyl chloride to alkenes has been studied in detail.[3,4] Recently, Schmid and Garratt[4] reported that the reaction may proceed like an S_N2 displacement process at bivalent selenium.[4] In the study of the addition of areneselenenyl chloride to (*E*)- and (*Z*)-1-phenylpropenes, they concluded that C–Se bond making lags behind the Se–Cl bond breaking in the rate-determining transition state.[4] If such argument is true, one may expect that Se–Br bond breaking would be more advanced than the Se–Cl bond cleavage when areneselenenyl bromide is employed in place of the corresponding chloride in the above reactions. To our surprise, little attention was given to elucidating the kinetics and mechanisms of the addition reactions with benzeneselenenyl bromide which seems to have been used more widely by synthetic organic chemists.[1] We now describe our findings on the kinetics of the addition of benzeneselenenyl bromide to substituted styrenes (eq 1).



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Results and Discussion

Kinetic Studies. All addition reactions were found to exhibit reversible second-order kinetics, first order in styrene and first order in benzeneselenenyl bromide to at least 80% completion of the reaction. The second-order rate constants for benzeneselenenyl bromide addition to substituted styrenes at 25 °C in benzene are summarized in Table I. Hammett plots against σ and σ^+ values give ρ and ρ^+ values of −0.37 (r = 0.975) and −0.27 (r = 0.967), respectively. The k_2's for the addition of benzeneselenenyl bromide to styrene at various temperatures are tabulated in Table II.

Table I. Second-Order Rate Constants for the Addition of Benzeneselenenyl Bromide to Substituted Styrenes in Benzene at 25 °C

substit	$10^2 k_2$,[a] $M^{-1}\ s^{-1}$
4-methoxy	3.55 ± 0.08 (3)
4-methyl	2.77 ± 0.1 (3)
none	2.58 ± 0.15 (5)
4-chloro	2.20 ± 0.1 (3)
3-chloro	1.57 ± 0.07 (3)
3-nitro	1.45 ± 0.002 (3)
4-nitro	1.41 ± 0.03 (3)

[a] Initial concentration of styrene = initial concentration of benzeneselenenyl bromide = 0.001 M. The number in the parentheses is the number of kinetic runs.

Table II. Temperature Dependence of k_2 for the Addition of Benzeneselenenyl Bromide to Styrene

T, °C	$10^2\ k_2^{obsd}$, $M^{-1}\ s^{-1}$
25	2.58
30	2.98
35	3.47
40	4.27

Table III. Enthalpies and Entropies of Activation for Some Electrophilic Additions to Styrene

electrophile	solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	ρ^+	ref
bromine	HOAc	12.5–12.8	−21.5 to −24.1	−4.3	6, 11
		6.1–9.0	−39 to −42		7
iodine thiocyanate	HOAc	7.7	−44	−2.59	8
2,4-dinitrobenzenesulfenyl chloride	HOAc	9.4–16.9[a]	−24.4 to −41.5	−2.20	8–10
benzeneselenenyl bromide	benzene	5.5	−47.2	−0.27	

[a] Data for *cis*- and *trans*-stilbene.

The Arrhenius plot (r = 0.994) gives $\Delta H^{\ddagger}$ = 5.54 kcal/mol and $\Delta S^{\ddagger}$ = −47.2 eu. The ρ^+ values and activation parameters are compared with related reactions (Table III).

Large negative $\Delta S^{\ddagger}$ values for the addition of benzeneselenenyl bromide to styrene strongly suggest that the reaction is bimolecular in nature. As shown in Table III,[5] the ρ^+ values is much less than those for related reactions

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[1] (a) Taken in part from the M. Phil. Thesis of W.H.S., 1980. (b) Summer undergraduate research participant, 1980.

[2] For reviews, see: (a) Liotta, D. *Acc. Chem. Res.* **1984**, *17*, 28. (b) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (c) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (d) Nicolaou, K. C.; Petasis, N. A. "Selenium in Natural Products Synthesis"; CIS: Philadelphia, 1984.

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[5] Although solvents used in the reactions shown in Table III are so different in polarity, a comparison is still meaningful because the mechanisms for these reactions are quite similar, namely, bimolecular in nature.

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Table IV. Product Compositions Determined in Various Solvents

	CCl_4		C_6D_6		$CDCl_3$	
substituent	1	2	1	2	1	2
4-methoxy	86	14	93	7	100	0
4-methyl	84	16	86	14	71	29
H	81	19	78	22	61	39
4-chloro	83	17	76	24	57	43
3-chloro	75	25	59	41	48	52
3-nitro	78	22	74	26	46	54
4-nitro	65	35	70	30	45	55

and those for the addition of areneselenenyl chloride to 1-phenylpropenes[4] and to substituted phenylethylenes ($\rho^+ = -2.23$).[4c] Our results establish that electron-donating groups in the phenyl ring of styrene only slightly enhance the rate of reaction. In other words, little positive charge is developed at the α carbon of styrene in the rate-determining transition state. There are two different possibilities to account for this observation. One is the rate-limiting step which corresponds to the formation of metastable tetravalent selenium species **3**. It is noted that tetravalent selenium compounds are generally more stable than analogous sulfur compounds.[12] Alternatively, the Se–Br bond breaking may be ahead of the C–Se bond formation in the rate-limiting transition state. Such nonsynchronous manner has been observed in the addition reactions with arenesulfenyl chloride[4,13] and with areneselenenyl chloride.[4] The limiting case would involve a competitive rate-determining selenium–halogen bond cleavage such that the overall rate constant would be much less dependent on the nature of the substituents on the aromatic ring. This argument seems to be compatible to our findings. Since bromide is in general a better leaving group than chloride, heterolytic dissociation of Se–Br bond would be more facile than that of Se–Cl bond. Indeed, the difference in ρ^+ values described above suggests that such dissociation step would be more significant in the addition reaction of benzeneselenenyl bromide to styrenes than that of benzeneselenenyl chloride to substituted phenylethenes. Our results support the idea[4] that C–Se bond making lags behind the Se–halogen bond breaking in the rate-determining transition state for the electrophilic addition of areneselenenyl halide to olefin.

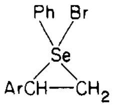
Product Distribution. The product compositions were determined by NMR spectroscopy. The assignment for chemical shifts of the protons of the products is based upon the fact that protons at α or β position to bromine are considerably deshielded relative to those at the α or β position to selenium.[6,7] In each case, the ratio of Markovnikov, **1**, to anti-Markovnikov products, **2**, is determined from the integration of at least one nonoverlapping signal.

The α proton of **1** is relatively deshielded compared to that of **2**. Thus the doublets of doublets at δ 4.95 and 4.44 are assigned to the protons of **1** and **2**, respectively. On the other hand, the β protons usually appear as doublets of doublets because of the splitting due to the asymmetric α carbon. Thus the set of doublets of doublets at δ 3.52 is assigned to the β protons of **1**, and that of **2** at δ 3.72. The chemical shifts for the α and β protons of the pairs of Markovnikov and anti-Markovnikov adducts are tabulated in Table V (supplementary material). The product compositions in various solvents are outlined in Table IV.

It is noted that the regioselectivity of the addition of benzeneselenenyl halide to olefins strongly depends on the temperature of the reaction.[16] Thus, at lower temperature, kinetic product or anti-Markovnikov adduct is generally obtained as the major product. On the other hand, at higher temperature, e.g., 25 °C, thermodynamic product predominates. In this study, similar conditions for kinetic measurements were employed for the study of the product distribution.

From Table IV, it can be seen that electron-withdrawing substituents on styrene give less regiospecific addition, i.e., the ratio of Markovnikov to anti-Markovnikov adducts approaches to 1. In the bridged transition state most of the positive charge is most likely localized on the Se atom; only a very small fraction of charge is distributed to the α and β carbons. Hence, the attack of Br^- would be nonregiospecific. On the other hand, electron-donating substituents such as methoxy or methyl groups could support a benzylic type of carbonium ion. The attack of Br^- would be mainly directed to the α carbon; thus the addition becomes more regiospecific. The major product would be Markovnikov adduct. The degree of bridging of the transition state should be higher for electron-withdrawing substituents than that for electron-donating substituents. A general trend was observed in which the ratio of Markovnikov to anti-Markovnikov adducts approaches 1 as the solvent polarity is increased.

In nonpolar solvents, the product-determining transition state may resemble contact ion pair **4**. Partial positive charge may develop at the α carbon and selenium. The attack of Br^- would thus favor the Markovnikov orientation. In polar solvents, the transition state may be solvated and resemble the solvent-separated ion pair **5** or free ion **6**.[14] The charge distribution at α and β carbons would be more symmetrical; the attack of Br^- would thus become nonregiospecific. A mixture of nearly equimolar amount of adducts would be formed.



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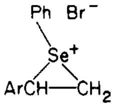

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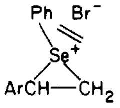

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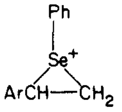

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The thermodynamically controlled products of the addition of 4-chlorobenzenesulfenyl chloride to styrene at 25 °C in 1,1,2,2-tetrachloroethane was found to be 100% Markovnikov orientated.[15] It is therefore suspected that the product-determining transition state in the 4-chlorobenzenesulfenyl chloride addition and benzeneselenenyl bromide addition to styrene would be quite different from each other. From the ρ values of these two reactions, the degree of bridging would be higher with selenium. In the case of benzeneselenenyl bromide addition to styrene, the product-determining transition state would be more bridged and the charge distribution would be more symmetrical. Therefore attack of Br^- would be nonregiospecific while in the case of 4-chlorobenzenesulfenyl chloride addition, the transition state would be less bridged.

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Table VI. ^{13}C NMR and ^{77}Se NMR[a] Chemical Shifts of the α and β Carbons and Selenium Nucleus of the Adducts in $\mathrm{CDCl_3}$

	1			2		
substrate	δ_{C_α}	δ_{C_β}	δ_{Se}	δ_{C_α}	δ_{C_β}	δ_{Se}
4-methoxy	55.3	35.2	−135.0	51.3[b]	34.5[b]	
4-methyl	52.7	36.2	−134.2	51.1	35.1	20.7
H	52.5	36.1	−134.2	47.6	35.2	25.4
4-chloro	51.3	36.0	−131.8	49.6	34.8	30.3
3-chloro	51.1	35.8	−132.7	46.8	34.5	31.7
3-nitro	50.0	35.4	−128.4	46.2	34.0	44.0
4-nitro	49.7	35.3	−129.8	46.4	33.8	48.8

[a] Diphenyl diselenide in $\mathrm{CDCl_3}$ as the external reference; positive values are downfield. [b] Measured in $\mathrm{C_6D_6}$.

In summary, strong support for the intermediacy of a bridged ion could be derived from $\sigma\rho$ relationships and $\Delta S^{\ddagger}$. Although a stable seleniranium ion has been prepared, the intermediate of the addition reaction seems not to involve the free seleniranium ion in nonpolar solvent.[14] Instead, the addition under nonpolar conditions would probably occur via less polar intermediates. In this regard, the selenenyl halide addition should be quite different from the sulfenyl halide addition.

^{77}Se and ^{13}C NMR Spectra. The products were also identified by employing ^{13}C NMR spectra as well as ^{77}Se NMR spectra at 17.08 MHz with diphenyl diselenide in $\mathrm{CDCl_3}$ as the external standard. The chemical shifts for the α and β carbons and the selenium nucleus of the adducts are summarized in Table VI. It is noteworthy that the effect of substituents on the ^{13}C shifts of the α and β carbons is small. For electron-withdrawing groups, the ^{13}C signals shifted upfield. Similar observation has been found in substituted diphenylmethanes.[17] There is no linear correlation between the ^{77}Se shifts in either adducts **1** or **2** and ^{13}C shifts of either α or β carbons. However, linear correlations (r = 0.9837) are found to exist between the ^{77}Se shifts in **2** and the σ values, and the slope (28.2) is less than that (43.7) for diphenyl selenide[16] which is obvious because the phenylselenenyl group in **2** is attached to the benzylic position of the substituted aromatic ring. Poorer correlation (r = 0.9435) was obtained when the ^{77}Se shifts of **1** were plotted against the σ values. Relatively smaller value for the slope (5.7) reflects that the effect of the remote substituent on the ^{77}Se shifts in **2** is small. Our results support the earlier suggestion that ^{77}Se shifts are much more sensitive to substituent than ^{13}C shifts.[17,18] In addition, the ^{77}Se NMR would be very useful in the identification of the isomer distribution as shown in this study.

Experimental Section

Melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer, ^{1}H NMR spectra on a JEOL 60 HL spectrometer, ^{13}C NMR and ^{77}Se NMR spectra on a JEOL FX 90Q spectrometer, and mass spectra on a VG 7070F mass spectrometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Commercially available styrene, 4-methylstyrene, and 3-nitrostyrene were distilled before use. Other substituted styrenes were prepared according to known procedures.[19] Benzeneselenenyl bromide was synthesized according to the literature method.[20] All solvents were purified according to standard procedures.[21]

Kinetic Studies. The rate of addition of benzeneselenenyl bromide to substituted styrenes in dry benzene at 25 °C was measured by spectrophotometric methods. The rate of disappearance of benzeneselenenyl bromide was followed by measuring the decrease in its absorption at 476 nm.

The second-order rate constants k_2 were obtained from the slope of the integrated expression for the reversible rate equation shown in eq 2 where x and x_e are the concentrations of adducts at time

$$k_2 t = \frac{x_e}{(ab - x_e^2)} \ln \frac{x_e(ab - x_e x)}{ab(x_e - x)} \qquad (2)$$

t and at equilibrium, respectively, and a and b are the initial concentrations of benzeneselenenyl bromide and styrene, respectively. Throughout this study initial concentrations for benzeneselenenyl bromide and styrene were both 0.001 M in benzene.

Product Distribution. A mixture of equimolar quantities of benzeneselenenyl bromide (1–2 mmol) and styrene (1–2 mmol) in the appropriate solvent was allowed to stand for several hours at 25 °C to achieve equilibrium. The NMR spectra of the adducts were recorded. The ratio of Markovnikov to anti-Markovnikov adducts was obtained from the integration of the peak areas of the protons α or β to the benzeneselenenyl group. The proton chemical shifts for the α and β protons of the adducts are summarized in Table 5. The ^{13}C NMR and ^{77}Se NMR chemical shifts for the α and β carbons, and selenium nucleus, respectively of the adducts **1** and **2** are outlined in Table VI. Attempts to separate the two isomers **1** and **2** were not successful.

Acknowledgment. We thank Mr. C. P. Yuen for measuring ^{13}C and ^{77}Se NMR spectra.

Registry No. PhSeBr, 34837-55-3; p-$\mathrm{MeOC_6H_4CH{=}CH_2}$, 637-69-4; p-$\mathrm{MeC_6H_4CH{=}CH_2}$, 622-97-9; $\mathrm{PhCH{=}CH_2}$, 100-42-5; p-$\mathrm{ClC_6H_4CH{=}CH_2}$, 1073-67-2; m-$\mathrm{ClC_6H_4CH{=}CH_2}$, 2039-85-2; m-$\mathrm{NO_2C_6H_4CH{=}CH_2}$, 586-39-0; p-$\mathrm{NO_2C_6H_4CH{=}CH_2}$, 100-13-0; p-$\mathrm{MeOC_6H_4CHBrCH_2SePh}$, 96999-51-8; p-$\mathrm{MeC_6H_4CHBrCH_2SePh}$, 96999-52-9; $\mathrm{PhCHBrCH_2SePh}$, 68001-60-5; p-$\mathrm{ClC_6H_4CHBrCH_2SePh}$, 96999-53-0; m-$\mathrm{ClC_6H_4CHBrCH_2SePh}$, 96999-54-1; m-$\mathrm{NO_2C_6H_4CHBrCH_2SePh}$, 96999-55-2; p-$\mathrm{NO_2C_6H_4CHBrCH_2SePh}$, 96999-56-3; p-$\mathrm{MeOC_6H_4CH(CH_2Br)SePh}$, 96999-57-4; p-$\mathrm{MeC_6H_4CH(CH_2Br)SePh}$, 97011-49-9; $\mathrm{PhCH(CH_2Br)SePh}$, 96999-58-5; p-$\mathrm{ClC_6H_4CH(CH_2Br)SePh}$, 96999-59-6; m-$\mathrm{ClC_6H_4CH(CH_2Br)SePh}$, 96999-60-9; m-$\mathrm{NO_2C_6H_4CH(CH_2Br)SePh}$, 96999-61-0; p-$\mathrm{NO_2C_6H_4CH(CH_2Br)SePh}$, 96999-62-1; Se-77, 14681-72-2.

Supplementary Material Available: Table V, showing the ^{1}H NMR chemical shifts of the α and β protons of the adducts in various solvents (1 page). Ordering information is given on any current masthead page.

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