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Mechanism of Hydrolysis of Vinyl Selenides and Stability of α-Selenocarbonium Ions

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Abstract: The mechanism of the acid-catalyzed hydrolysis of a number of methyl vinyl selenides has been investigated. For all the compounds kinetic solvent isotope effects $k_{H_3O^+}/k_{D_3O^+}$ ranged from 1.4 to 1.8. It was also shown that a substantial amount of substrate isomerization and deuterium incorporation occurred during hydrolysis. These results contrast with those reported for vinyl ethers, vinyl sulfides, and phenyl vinyl selenides and show that a different hydrolysis mechanism pertains for methyl vinyl selenides. The important features of this mechanism are a partially reversible initial slow protonation step and the possibility of accumulation of the hemiselenoacetal intermediate. Stabilization of the carbonium ion intermediate by a methylseleno group as well as the accumulation of the hemiselenoacetal are the factors responsible for the observed partial reversibility. It was also shown by the deuterium incorporation experiments that phenyl vinyl selenides are also susceptible for reversible protonation provided they bear an alkyl or aryl substituent at the α-position of the vinyl moiety. Therefore, all vinyl selenides hydrolyze by this mechanism except unsubstituted aryl vinyl selenides. The greater ability of an α-methylseleno group to stabilize carbonium ions relative to that of an α-phenylseleno group is reflected in the hydrolysis rate ratio (CH_3Se/C_6H_5Se = 15) of the corresponding vinyl selenides. This ratio when compared to literature data (CH_3O/C_6H_5O = 133 and CH_3S/C_6H_5S = 41) shows that carbonium ion stabilizing interactions are substantially but not drastically reduced when going from oxygen to sulfur and to selenium substituents.

The mechanism of hydrolysis or hydration of numerous vinylic substrates has been thoroughly investigated in recent years. These substrates include olefins,[3] vinyl ethers,[4] vinyl sulfides,[5] 1-alkynyl sulfides,[6] and *N*-vinyl acetamides,[7] and it has been shown for all of them that the hydration or hydrolysis reactions proceed by rate determining and irreversible proton transfer from hydronium ion or general-acid catalysts to the β-carbon atom of the olefinic linkage.

During the past decade organoselenium derivatives have been revealed as useful synthetic intermediates.[8] From this point of view one interesting property of α-alkyl- or α-arylseleno moieties is their ability to stabilize carbanionic species in a way and to an extent quite comparable to the corresponding thio groups.[9]

While the stabilization of carbonium ions by divalent oxygen and sulfur atoms is a well-documented subject,[10,11] until recently only limited information was available regarding the stability of α-selenocarbonium ions.[12] The hydrolysis of aryl vinyl selenides[13] and that of an aliphatic methyl vinyl selenide[14] were briefly described.

We report here a more detailed study of the mechanism of hydrolysis of both types of vinyl selenides as well as rate measurements which along with literature data allow us to point out the difference in the liquid phase between the carbonium ion stabilizing abilities of α-oxo, -thio and -seleno groups.

Experimental Section

Reagents. All organic reagents and solvents including the deuterated ones were purchased from Aldrich Europe (Beerse, Belgium) or from Merck (Darmstadt). Tap water was deionized and then bidistilled in an all quartz apparatus before use in the kinetic measurements. Perchloric acid (Merck) was an analytically pure product. 1,4-Dioxane (Merck) of analytical grade was refluxed over sodium for several hours and then distilled before use.

Vinyl selenides have been prepared by reacting the corresponding selenoacetals with methyl iodide according to methods worked out in our laboratory.[15] The reactions are usually performed at 80 °C in anhydrous dimethylformamide except for α-methylselenostyrenes whose formation requires a lower reaction temperature (~20 °C).

Stereochemically pure (*E*)- and (*Z*)-2-(methylseleno)-2-tridecenes were synthesized via the corresponding β-hydroxy-α-silyl methyl selenides as already described.[16]

Methyl vinyl selenide was obtained from ethylene and methyl selenenyl bromide and further reaction formed β-bromo selenide with *t*-BuOK (freshly sublimed) in THF.[17,18]

^1H NMR spectra were recorded on a JEOL MH-100 (100 MHz) instrument while ^{13}C and ^{77}Se NMR spectra were obtained by means of

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[1] Part of this work is taken from J. L. Piquard, Mêmoire de licence, University of Namur, 1979.

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a JEOL FX 90Q (90 MHz for proton) spectrometer mounted with a tunable multinuclear probe.

All vinyl selenides are pale yellow liquids; their analytical data are as follows.

(*Z*)-2-(Methylseleno)-2-tridecene: ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 5.46 (t, J = 7 Hz, 1 H, $-CH{=}C$), 2.01 (m + s, 8 H, $-CH_2{-}CH{=}C$, $-Se{-}CH_3$, and $C{=}C\text{-}CH_3$), 1.22 (m, 16 H, $-(CH_2)_8{-}CH_2{-}C{=}C$), 0.87 (t, J = 6.5 Hz 3 H, $-(CH_2)_9{-}CH_3$); IR (liquid film) 2960, 2920, 2860, 1635, 1470, 1380, 1275, 910 cm^{-1}; mass spectrum, (*m/e*) 276 (M^+), 261 ($M^+ - CH_3$), 149 ($M^+ - C_9H_{19}$); UV (dioxane) λ_{max} 243 (ϵ = 2530), 263 nm (sh ϵ = 1390).

Anal. Calcd: C, 61.07; H, 10.25. Found: C, 61.04; H, 10.42.

(*E*)-2-(Methylseleno)-2-tridecene: ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 5.41 (t, J = 6.5 Hz, 1 H, $-CH{=}C$), 2.02 (m + s, 5 H, $-CH_2{-}C{=}C$ and $-Se{-}CH_3$), 1.97 (s, 3 H, $CH_3{-}C{=}C$), 1.24 (m, 16 H, $-(CH_2)_8{-}CH_2{-}C{=}C$), 0.89 (t, J = 6.5 Hz, 3 H, $-(CH_2)_9{-}CH_3$); IR (liquid film) 2920, 2860, 1635, 1470, 1380, 1270, 905 cm^{-1}; mass spectrum same as the *Z* isomer; UV (dioxane) λ_{max} 248 (ϵ = 2520), 263 nm (sh, ϵ = 1190).

Anal. Calcd: C, 61.07; H, 10.25. Found: C, 61.80; 10.37.

α-(Methylseleno)-*p*-nitrostyrene: ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 7.90 (center of aromatic AB quarter, J = 8 Hz, 4 H), 5.84 (s, 1 H, olefinic proton cis to phenyl ring), 5.40 (s, 1 H, olefinic proton trans to phenyl ring), 2.10 (s, 3 H, $-Se{-}CH_3$); ^{13}C NMR (CCl_4 δ(Meq Si) 147.53, 147.15, 123.70 (aromatic carbons), 139.95 ($C{=}CH_2$), 116.22 ($C{=}CH_2$), 7.15 ($Se{-}CH_3$); mass spectrum, *m/e* 243 (M^+), 148 ($M^+ - SeCH_3$).

α-(Methylseleno)-*p*-chlorostyrene: ^{1}H NMR (CCl_4) δ(Meq Si) 7.31 (center of aromatic AB quarter, J = 9 Hz, 4 H), 5.65 (s, 1 H, olefinic proton cis to phenyl ring), 5.20 (s, 1 H, olefinic proton trans to phenyl ring), 2.02 (s, 3 H, $-SeCH_3$); UV (dioxane/water, 60/40 v/v) λ_{max} 241 (ϵ = 11 100), 282 nm (sh, ϵ = 2520).

α-(Methylseleno)styrene: ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 7.20–7.56 (m, 5 H, aromatic), 5.68 (s, 1 H, olefinic cis to phenyl), 5.20 (s, 1 H, olefinic trans to phenyl), 2.01 (s, 3 H, $-SeCH_3$); mass spectrum, *m/e* 198 (M^+), 103 ($M^+ - SeCH_3$), 77 ($C_6H_5^+$).

Anal. Calcd: C, 54.84; H, 5.11. Found: C, 55.08; H, 5.21.

α-(Methylseleno)-*p*-methylstyrene: ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 7.13 (center of aromatic AB quarter, J = 8 Hz, 4 H), 5.59 (s, 1 H), 5.12 (s, 1 H, olefinic protons cis and trans to phenyl, respectively), 2.18 (s, 3 H, $-C_6H_4{-}CH_3$), 1.99 (s, 3 H, $-Se{-}CH_3$); mass spectrum, *m/e* 2.12 (M^+), 117 ($M^+ - SeCH_3$), 91 ($C_6H_4{-}CH_3$); UV (dioxane/water, 60/40 v/v) λ_{max} 244 (ϵ = 20 500), 282 nm (sh, ϵ = 3550).

Anal. Calcd: C, 56.88, H, 5.73. Found: C, 56.65; H, 5.65.

α-(Methylseleno)-*p*-methoxystyrene: ^{1}NMR (CCl_4) $\delta(Me_4Si)$ 7.08 (center of aromatic AB quartet, J = 8 Hz, 4 H), 5.60 (s, 1 H), 5.12 (s, 1 H, olefinic protons cis and trans to phenyl ring, respectively), 3.72 (s, 3 H–OCH_3), 2.00 (s, 3 H, $-SeCH_3$); UV (dioxane/water, 60/40 v/v) λ_{max} 2.52 (ϵ = 12 650), 282 (sh, ϵ = 5600).

α-(Phenylseleno)styrene: ^{1}NMR δ 7.1–7.6 (m, 10 H, aromatic), 5.80 (s, 1 H) and 5.28 (s, 1 H), (olefinic protons); mass spectrum, *m/e* 260 (M^+), 103 ($C_6H_5{-}C^+{=}CH_2$), 77 ($C_6H_5^+$); UV (dioxane) λ_{max} 248 (ϵ_{max} = 10 600), 263 nm (sh, ϵ = 7500).

Methyl Vinyl Selenide. Ethylene was allowed to react at 0 °C with 9.4 g (5×10^{-2} M) of dimethyl diselenide and 8 g (5×10^{-2} M) of bromine dissolved in 100 mL of dichloromethane. The initially black solution decolorized to pale yellow within a few minutes. The solution was filtered to eliminate the small amount of red selenium formed in the reaction. Evaporation of the solvent yielded 20 g (~99%) of 1-bromo-2-(methylseleno)ethane, a pale yellow liquid which was used without further purification: ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 3.40–3.57 (m, 24, $Br{-}CH_2{-}$), 2.78–2.96 (m, 2 H, $-CH_2{-}SeCH_3$), 1.98 (s, 3 H, $-Se{-}CH_3$).

This compound was then treated with 1 equiv of *t*-BuOK in THF for 1 h at 0 °C and 1 h at room temperature. Methyl vinyl selenide was distilled out of the reaction mixture together with THF and some *tert*-butyl alcohol. Ether was added and the solution was washed with sodium bicarbonate and water. Distillation on a spinning-band apparatus yielded methyl vinyl selenide as a pale yellow liquid (bp_{760} 88 °C): ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 6.80 (dd, J_1 = 10 Hz, J_2 = 17 Hz, 1 H $-CH{=}C$), 5.66 (d, J_1 = 10 Hz, 1 H) and 5.23 (d, J = 17 Hz, 1 H) ($-CH{=}CH_2$), 2.04 (s, 3 H, $-SeCH_3$); UV (dioxane) λ_{max} 241 (ϵ_{max} = 9400), 275 nm (sh, ϵ_{max} = 2900).

(Phenylseleno)-2-propane was prepared from the corresponding selenoacetal:[15] ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 7.2–7.7 (m, 5 H, $-Se{-}C_6H_5$), 5.42 (b s, 1 H) and 5.08 (s, 1 H) ($C{=}CH_2$), 2.01 (s, 3 H, $-CH_3$).

α-(Phenylseleno)-*p*-nitrostyrene was prepared from the corresponding selenoacetal:[15] ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 7.81 (center of aromatic AB quartet, J = 8 Hz, 4 H), 7.1–7.5 (m, 5 H, $-Se{-}C_6H_5$), 5.90 (s, 1 H), 5.50 (s, 1 H, $C{=}CH_2$).

***O*,*Se*-Dimethylacetal of *p*-nitroacetophenone** was obtained by treating the corresponding *O*,*O*-acetal with 1 equiv of methaneselenol in carbon tetrachloride containing ~0.05 equiv of sulfuric acid: ^{1}H NMR ($CDCl_3$) $\delta(Me_4Si)$ 7.95 (center of aromatic AB quartet J = 8 Hz, 4 H), 3.42 (s, 3 H, OCH_3), 1.85 (s, 3 H, $\equiv C{-}CH_3$), 1.56 (s, 3 H, $-SeCH_3$); ^{13}C NMR ($CDCl_3$) $\delta(Me_4Si)$ 153.06 and 146.51 (aromatic quaternary carbons), 126.73 and 123.04 (other aromatic carbons), 86.85 (benzylic carbon), 51.85 (OCH_3), 27.25 ($\equiv C{-}CH_3$), 3.20 ($-SeCH_3$); ^{77}Se NMR (CH_3OH) $\delta(CH_3SeCH_3)$ 308.

***O*,*Se*-Dimethylacetal of 2-tridecene** was prepared from the corresponding *O*,*O*-dimethylacetal on treatment with $B(SeCH_3)_3$ in dichloromethane solution at room temperature. The crude product was purified by chromatography on buffered (pH 7) silica gel plates (eluant ether/pentane, 5/95 v/v): ^{1}H NMR (CCl_4) $\delta(Me_4Si)$ 3.16 (s, 3 H, $-OCH_3$), 1.74 (s + m, 5 H, $-SeCH_3$ and $\equiv C - CH_2{-}$), 1.46 (s, 3 H, $\equiv C{-}CH_3$), 1.22 (m, 18 H, $CH_3\text{-}(CH_2)_9{-}$), 0.87 (t, J = 6 H, 3 H, $CH_3{-}(CH_2)_{10}{-}$); UV (dioxane) λ_{max} 230 nm (ϵ_{max} = 221).

Product Analysis

Hydrolysis of 2-(methylseleno)-2-tridecene has been effected in conditions similar (except for concentrations) to those of the kinetic measurements. A 276-mg (10^{-3} mol) sample of the vinyl selenide was stirred vigourously in a mixture of 6 mL of dioxane and 4 mL of water containing 2 g (2×10^{-2} M) of perchloric acid for 1 day. The reaction mixture was extracted with ether, washed several times with water, dried over $MgSO_4$, and evaporated. Purification of the crude product on PLC (SiO_2, ether/pentane, 10/90 v/v; R_f 0.48) yielded 194 mg (97%) of 2-tridecanone identified by its NMR and IR spectra.

α-(Methylseleno)styrene hydrolyzed smoothly under conditions similar to the above. However, besides substituted acetophenones, the crude products contained variable amounts (7% for α-(methylseleno)-*p*-nitrostyrene and 30% for α-(methylseleno)styrene) of the corresponding (methylseleno)acetals. We believe these side reactions are due to the high vinyl selenide concentration initially present in the reaction mixtures. Under more dilute and aerobic conditions methylselenol formed in the early stages of the hydrolysis reaction is oxidized to diemthyl diselenide and cannot therefore add to the unreacted vinyl selenide. This was confirmed by UV spectra recorded at the end of the kinetic runs, which showed exclusively characteristic absorption of the acetophenones.

Isomerization during Hydrolysis. A 10-mg (3.64×10^{-5} M) sample of 2-(methylseleno)-2-tridecene was dissolved in 10 mL of dioxane/water (60/40 v/v; 0.29 M in $HClO_4$) and allowed to react at room temperature for 3.5 h. After being quenched with base, the reaction mixture was extracted with ether, washed, dried, concentrated, and submitted to gas chromatographic analysis (Perkin-Elmer Sigma-3, mounted with a high loading SE-30 glass capillary column of 50-m length and 0.5-mm internal diameter). The chromatogram showed the following peaks which were identified by means of authentic samples (retention time t_r in minutes): 2-tridecanone (4.7), *cis*-2-(methylseleno)-2-tridecene (12.5), 2-(methylseleno)-1-tridecene (12.7), and *trans*-2-(methylseleno)-2-tridecene (13.7).

Interpretation of this spectrum showed that the reaction has attained 21% conversion, and the unreacted vinyl selenide was composed of 57.9% of cis isomer, 32.7% of trans isomer, and 9.4% of 2-(methylseleno)-1-tridecene. The total isomer interconversion was therefore 42.1% [(i.e., (trans + exo)/(cis + trans + exo)].

Several analyses of this type were carried out under different reaction conditions, and all showed substantial isomer interconversion. In the same way, thermodynamic equilibration of a synthetic mixture of *cis*- and *trans*-2-(methylseleno)-2-tridecene (59% and 41%, respectively) was effected in dry methanol and in the presence of a catalytic amount of *p*-toluenesulfonic acid. After 24 h, the cis/trans ratio changed from 59/41 to 45/55.

Deuterium Incorporation. A 100-mg (4×10^{-4} M) sample of the synthetic mixture of 2-(methylseleno)-2-tridecene was dissolved in 25 mL of dioxane D_2O (60/40 v/v, 0.8 M in DCl) and allowed to hydrolyze for 4 h. The usual quenching and extraction was followed by purification of the crude reaction mixture on preparative SiO_2 plates (eluant pentane). This yielded 56 mg of 2-tridecanone and 7 mg of unreacted vinyl selenides. Comparison of the mass spectrum of this latter (M^+ and $M^+ + 1$ peaks) with that of the starting material showed that about 25% of the unreacted vinyl selenides contained one deuterium atom. Deuterium

Table I. Observed (Pseudo-First-Order) Rate Constants for the Hydrolysis of *cis*-2-(Methylseleno)-2-tridecene as a Function of Catalyst ($HClO_4$) Concentration[a]

$HClO_4$, M	H_0	k_{obsd}, s^{-1}	no. of runs
0.25	1.90	9.09×10^{-6}	8
0.50	1.40	3.13×10^{-4}	4
1.00	0.75	2.12×10^{-3}	5
1.50	0.22	9.22×10^{-3}	6
2.00	−0.26	3.54×10^{-2}	5

[a] T = 30 °C; solvent dioxane/water, 60/40 v/v.

Table II. Effect of Temperature on the Rate of Hydrolysis of *cis*-2-(Methylseleno)-2-tridecene in Dioxane/Water[a]

T, °C	$10^3 k_{obsd}$, s^{-1}	no. of runs	dev, %
50	9.43	5	5.4
45	6.55	4	3.2
40	4.54	6	2.2
35	3.21	4	0.9
30	2.12	5	2.9

[a] 60/40 v/v; 1 M in $HClO_4$.

incorporation by the other vinyl selenides has been evaluated similarly.

Kinetic Measurements. Rates of hydrolysis were measured spectrophotometrically (Pye Unicam 1800, provided with a thermostatable cell holder) by following the disappearance of the starting material (or sometimes the appearance of the ketonic product) for 3–4 half lives. Absorbances at infinite time were recorded after 10–12 half lives. The reactions were initiated by adding 0.1 mL of a stock solution (dioxane) of the vinyl selenide to 4 mL of the thermostated reaction mixture. Pseudo-first-order conditions were used, and the observed rate constants were calculated by using a mean-squares program.

Results and Discussion

Hydrolysis of 2-(Methylseleno)-2-tridecene. Both Z and E isomers of the title compound have been prepared and their rates of hydrolysis measured at 30 °C in the solvent system dioxane/water (60/40 v/v). At 1 M $HClO_4$ catalyst concentration, we have found that *cis*-2-(methylseleno)-2-tridecene reacts 1.3 times faster than the trans isomer. Similar observations have already been described for the related vinyl ethers[4m] and vinyl sulfides.[5a] The effect of catalyst concentration on the rate of hydrolysis has been examined only in the case of the cis isomer; the results are collected in Table I.

Mean-squares analysis of these data showed an excellent linear dependence of the logarithm of k_{obsd} on the Hammet acidity function[19] (H_0 of the reaction medium). The correlation is described by eq 1. Activation parameters for the hydrolysis of the

$$\log k_{obsd} = -0.011\ (\pm 0.001) - 1.21\ (\pm 0.078) H_0 \qquad (1)$$

same isomer have been determined by rate measurements at temperatures ranging from 30 to 50 °C (Table II). The data fit perfectly into the Arrhenium equation which gives $\Delta H^{\ddagger}$ = 13 kcal M^{-1} and $\Delta S^{\ddagger}$ = −25 eu. The figures obtained so far are typical for the hydration on hydrolysis of vinylic substrates.[2-5] However, despite of this similarity, the mechanism of hydrolysis of vinyl selenides cannot be accepted as identical with that of vinyl ethers and vinyl sulfides. This is shown inter alia by kinetic solvent isotope effects, which have been determined at 30 °C by measuring the rates of the reaction in the usual dioxane/water mixture in which the water fraction was pure H_2O, pure D_2O, or a 50/50 v/v mixture of them. The catalyst was HCl or DCl. These results are shown in Table III, where the ratio $k_{H^3O}/k_{D_3O^+}$ = 1.38. This is a rather astonishing observation which seems to indicate a rate-determining protonation step (ratio > 1). However, its numerical value is substantially lower than that observed for vinyl ethers and vinyl sulfides[4,5] (typically ~3). If the usual mechanism pertains to slow and irreversible proton transfer to the β-carbon of the olefinic bond, there is no a priori reason why $k_{H_3O^+}/k_{D_3O^+}$ should change by more than a factor of 2 on replacing oxygen or sulfur by a selenium atom in the vinylic substrate. The observed relatively low-limiting solvent isotope effect suggests therefore a change in mechanism of hydrolysis of our vinyl selenide.

Table III. Solvent Isotope Effects in the Hydrolysis of *cis*-2-(Methylseleno)-2-tridecene[a]

water fraction of solvent	HCl or DCl, M	$10^3 k_{obsd}$, s^{-1}	no. of runs
D_2O	0.982	1.25	4
H_2O	0.980	1.73	4
H_2O/D_2O (50/50)	0.983	1.64	2

[a] T = 30 °C; solvent dioxane/water (or D_2O), 60/40 v/v.

The nature of the first protonation step was clearly unveiled by studying deuterium incorporation and isomer interconversion during hydrolysis. The latter was shown to take place under several experimental conditions (nature and concentration of catalyst). One example is described here (see Experimental Section) which pertains to the hydrolysis of *cis*-2-(methylseleno)-2-tridecene. The reaction was monitored by gas chromatography. Figure 1 shows the chromatogram obtained after 3.5 h of reaction (corresponding to an estimated 21% conversion) as compared to that of the starting material. It can be seen that the unreacted and initially pure cis vinyl selenide underwent a very significant isomerization since the vinyl selenide fraction is estimated (by peak area calculation) to contain 57.9% of cis, 32.7% of trans, and 9.4% of exo isomer 2-(methylseleno)-1-tridecene.

The same type of experiment was also performed on a mixture of cis and trans vinyl selenides in dioxane/D_2O (60/40 v/v) in the presence of DCl catalyst. When the catalyst concentration was 0.8 M, the reaction reached about 90% conversion after 4 h. The reaction was then quenched, and the product was extracted and analyzed. We found it contained mostly 2-tridecanone and a small amount (~10%) of unreacted vinyl selenide, which was examined by mass spectrometry, and the mass spectrum was compared to that of a reference starting material. The most striking feature of the mass spectrum of the recovered vinyl selenides was the presence of an M + 1 peak of much higher intensity than the corresponding peak of the reference vinyl selenides. Peak height measurements showed that about 25% of the vinyl selenides recovered from the reaction medium did incorporate one deuterium atom.

Thus these two experiments, isomer interconversion and deuterium incorporation, corroborate each other and show undoubtedly that under the conditions of hydrolysis an equilibrium exists between the starting vinyl selenide and the corresponding α-(methylseleno)carbonium ion. To our knowledge, this phenomenon is for the first time observed for the hydrolytic reactions of an α-hetero-substituted olefin.

However, the observed solvent isotope effect ($k_{H_3O^+}/k_{D_3O^+} \simeq$ 1.4) does not correspond to a rapid equilibrium protonation step. Moreover, although it is not possible to know the equilibrium constant between the cis and trans isomers of 2-(methylseleno)-2-tridecene under the reaction conditions, we have some indications that the observed isomeric ratio after 3.5 h (~20% conversion) of reaction does not correspond to the equilibrium distribution. For example, the percentage of total isomerization [(trans + exo)/(cis + trans + exo)] increases with the reaction time. Thus the hydrolysis of the cis isomer in dioxane/water (60/40 v/v) in the presence of 1 M triflate buffer (pH 1.2) shows after 4 and 9 h of reaction 10.6% and 15.5% of total isomerization respectively.[20] We also observed that, starting from a synthetic mixture of *cis*- and *trans*-2-(methylseleno)-2-tridecene (59% and (41%, respectively), equilibration in dry methanol in the presence of a small amount of p-toluenesulfonic acid yielded after 24 h vinyl

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(19) H_0 values for perchloric acid in dioxane/water (60/40 v/v) were taken from M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1–45 (1957).

(20) The limiting value, i.e., the percentage of total isomerization near the end of reaction, would probably be a good estimate of the global equilibrium constant for isomerization in a given medium.

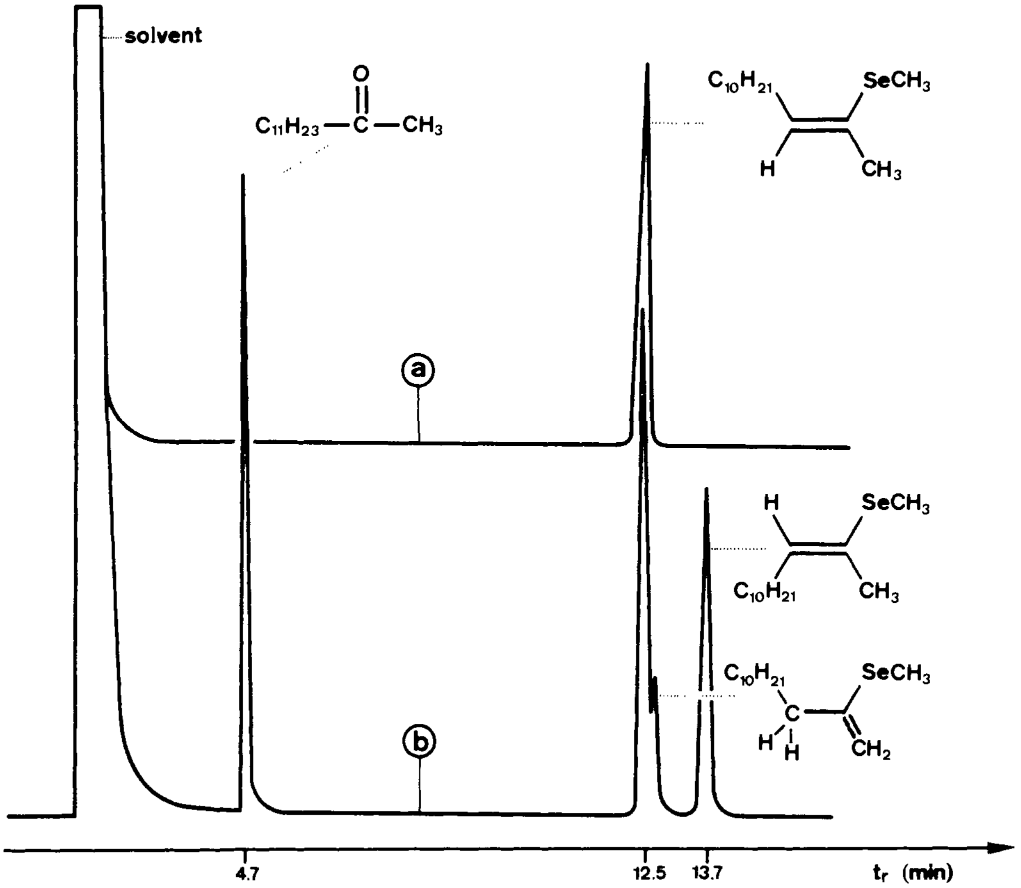


Figure 1. Chromatogram (a) of the starting material (*Z*)-2-(methylseleno)-2-tridecene (1) and (b) of the reaction mixture after 3.5 h of hydrolysis in dioxane/water (60/40 v/v; 0.29 M in HClO).

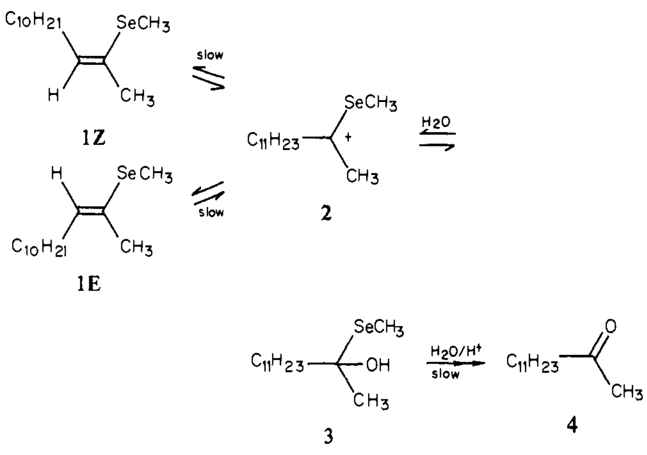
selenide in which the cis/trans ratio was 45/55. As far as acidic methanol is comparable to the hydrolysis medium, the isomer ratio determined in the course of the reaction differs from the equilibrium ratio. Finally, if the protonation step occurred under a rapid equilibrium, deuterium incorporation into the unreacted vinyl selenide had to be complete. This was never observed.

Consequently, initial protonation of the vinyl selenide 2-(methylseleno)-2-tridencene appears to be a reversible but slow step, which allows for partial isomerization and partial deuterium incorporation into the remaining vinyl selenide. It follows that the mechanism of hydrolysis of this vinyl selenide should be as depicted in Scheme I.

This mechanism is in contrast with that proposed recently[13] by McClelland and Leung. These authors have investigated the mechanism of hydrolysis of para-substituted phenyl vinyl selenides and compared their reactivities to those of the oxygen and sulfur analogues. They found that hydrolysis of the unsubstituted derivative shows a normal solvent isotope effect of $k_{H_3O^+}/k_{D_3O^+} = 2.9$, which together with other kinetic features of the reaction points to the A-S_E2 mechanism. We confirmed this result by carrying out our deuterium incorporation experiment on phenyl vinyl selenide. Within the limits of precision of the mass spectrometric determination, we could not observe any incorporation of deuterium into the recovered unreacted vinyl selenide neither after 30% nor after 60% conversion. We are therefore faced with a class of compounds for which a modification of structure not only changes rates but also brings about a change in the reaction mechansim.

Although precise pK_a values for selenides and selenoacetals are not available, it can be inferred by analogy with sulfur[21] that proton basicity of the selenium atom of intermediate **3** (Scheme I) should be very low. It follows that compared to its rate of formation, decomposition of this intermediate could be a slow process; therefore, it could accumulate during hydrolysis. To confirm this, we have prepared 2-methoxy-2-(methylseleno)tridecane, a model for **3**, and measured its rate of hydrolysis in dioxane/water (60/40 v/v; 1 M in HClO$_4$) at 30 °C. We found it to hydrolyze approximatively 10 times slower than did vinyl selenide **1** under the same conditions. As far as the *O,Se*-dimethylacetal is a good model for **3**, this result implies that **3** must accumulate at least to some extent during the hydrolysis of vinyl selenide **1**. Such an accumulation may be one reason for the partial reversibility of the initial proton-transfer step.

Scheme I



Hydrolysis of α-(Methylseleno)styrene. In the light of the results obtained for 2-(methylseleno)-2-tridecene, we wanted to investigate further the effect of vinyl selenide structure on the mechanism of hydrolysis. Therefore, we have also studied solvent

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(21) P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 2267 (1972); P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **95**, 5960 (1973).

Table IV. Solvent Isotope Effects and Deuterium Incorporation[a] for Para-Substituted α-(Methylseleno)styrenes $p\text{-X-C}_6H_4\text{-C(SeCH}_3)\text{=CH}_2$

X	$10^4 k_{H_3O^+}$, s^{-1}	$10^4 k_{D_3O^+}$, s^{-1}	$k_{H_3O^+}/k_{D_3O^+}$	% D incorptn[a]
CH_3O-	727	435	1.67	
CH_3-	203	117	1.74	17
H-	75.8	42.7	1.79	31
Cl-	34.5	19.3	1.78	
NO_2	1.92	1.21	1.59	40

[a] Percentage of vinyl selenide recovered (after ~50% conversion) which has incorporated one deuterium atom, determined as in the preceding section. Dioxane/water, 60/40 v/v; 1.25 M in HCl or DCl; $T = 30$ °C.

isotope effects and deuterium incorporation in the case of para-substituted α-(methylseleno)styrenes. Results of these experiments are gathered in Table IV.

The data of Table IV show that both solvent isotope effects and deuterium incorporations for all the para-substituted derivatives are quite similar to those of the aliphatic methyl vinyl selenide 2-(methylseleno)-2-tridecene **1** and point therefore to the same mechanism. It also appears from Table IV that the percentage of deuterium incorporation increases with decreasing overall hydrolysis rate. This is also in agreement with a slow but reversible first protonation step as pictured in Scheme I. The partially rate-limiting nature of this step is dictated by the observed $k_{H_3O^+}/k_{D_3O^+}$ ratios (Table IV) as well as by the fact that the observed rate constants $k_{H_3O^+}$ are satisfactorily correlated to σ and σ^+ parameters by the Yukawa-Tsuno eq[22] 2 and 3.

$$\log (k/k_0)_{H_3O^+} = -2.03[\sigma + 0.4(\sigma^+ - \sigma)] \quad (2)$$

$$\log (k/k_0)_{D_3O^+} = -1.98[\sigma + 0.4(\sigma^+ - \sigma)] \quad (3)$$

However, no satisfactory correlation could be obtained by using σ or σ^+ parameters alone. This means that the transition state for proton transfer into these vinyl selenides has a considerable but not a full carbonium ion character.

We have also considered the possibility of accumulation of a hemiselenoacetal intermediate of type **3** (Scheme I) during the hydrolysis of the α-(methylseleno)styrenes. Due to its instability, such an intermediate would be difficult or impossible to isolate even in case of a high degree of accumulation. We chose therefore to simulate hydrolysis by methanolysis of the vinyl selenide, and we monitored the reaction by ^{13}C and ^{77}Se NMR spectroscopy. Figure 2 shows the evolution with time of the proton broad-band decoupled ^{77}Se spectra of 120 mg ($\simeq 5 \times 10^{-4}$ mol) of α-(methylseleno)-*p*-nitrostyrene in 1 mL of methanol containing 200 mg (~4 equiv) of sulfuric acid. Five selenium-containing species can be identified in these spectra: methaneselenol (−131.7 ppm), dimethyl diselenide (+270.3 ppm), α-(methylseleno)-*p*-nitrostyrene (+235.1 ppm), (methylseleno)acetal of *p*-nitroacetophenone (+386.6 ppm), and the mixed *O,Se*-dimethylacetal of *p*-nitroacetophenone (+310.9 ppm). The last compound has been identified by its independent synthesis. When the authentic *O,Se*-dimethylacetal was placed in the same conditions as the above vinyl selenide, the ^{77}Se NMR spectrum resembled closely after 2 h of methanolysis the one given in Figure 2D, the only differences being in the relative intensities of the species present in the mixture and a change of ~0.5 ppm in the respective chemical shifts. The latter is negligible when account is taken of the high-temperature sensitivity of ^{77}Se chemical shifts.[23] Although these observations do not prove that the intermediate hemiselenoacetal accumulates during hydrolysis, they show that such an accumulation is possible under favorable experimental conditions and that decomposition of the intermediate may not be rapid as compared to the initial protonation step.

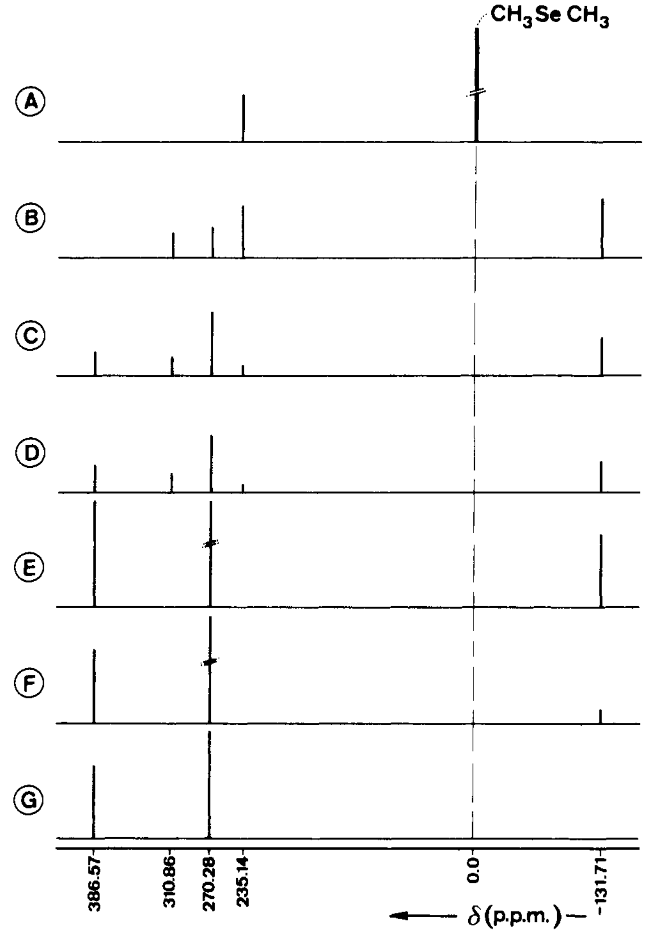

Figure 2. ^{77}Se NMR spectra of α-(methylseleno)-*p*-nitrostyrene (5×10^{-4} mol) in methanol (A) without acid and (B–G) in the presence of 2×10^{-3} mol of H_2SO_4 after 45, 70, 120, 165, 270, and 370 min, respectively. Spectra A–D were obtained from 300 scans and E–G resulted from 2000 scans.

Moreover, 5 min after the mixed *O,Se*-dimethylacetal of *p*-nitroacetophenone was dissolved in acidic methanol, ^{77}Se NMR spectra revealed the presence of a large amount of methaneselenol. Taken nearly at the same time, the ^{13}C NMR spectrum showed the formation of a large amount of the corresponding *O,O*-acetal and no traces of the *Se,Se*-acetal. The latter appeared in the spectra after 1–1.5 h of reaction, which means that C–Se bond cleavage in the mixed *O,Se*-acetal occurs faster but not much faster than C–O bond cleavage. This observation parallels that of Jensen and Jencks regarding the position of bond cleavages in mixed *O,S*-acetals[24] and the structural features which govern them.

Summarizing the results of McClelland and Leung[13] and those described above, we can conclude that the mechanism of hydrolysis of vinyl selenides is most sensitive to the nature of the selenium moiety. Phenyl vinyl selenides hydrolyze according to the classival A2 mechanism, while all the methyl vinyl selenides studied by us react by an A2-type mechanism which involves a partially reversible protonation step and a possibly slow decomposition step of the intermediate hemiselenoacetal. Interestingly, parasubstituents neither in phenyl vinyl selenides nor in α-(methylseleno)styrenes are capable of changing the corresponding reaction mechanism. This suggests that the ability of the selenium moiety to stabilize a carbonium ion intermediate plays a more fundamental role in determining the mechanism than its basicity on which depends the rate of decomposition of the hemiselenoacetal intermediate of type **3**. It is indeed quite clear that a methylseleno group stabilizes a positive charge better than does a phenylseleno

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(22) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reaction", Wiley, New York, 1963.

(23) See for example: C. Rodger, N. Sheppard, H. C. E. McFarlane, and W. McFarlane in "NMR and the Periodic Table", R. K. Harris and B. E. Mann, Eds., Academic Press, London, 1978, p 404. On our own, we have observed a variation of 0.3 ppm per °C of $\delta(^{77}Se)$ for bis(dimethylseleno)methane in THF solution in the temperature range of −80 to +20 °C.

(24) J. L. Jensen and W. P. Jencks, *J. Am. Chem. Soc.*, **101**, 1476 (1979).

Table V. Percentage of Deuterium Incorporation and Hydrolysis Rate Constants of Selected Vinyl Selenides

compd	% D incorptn[a]	$k_{H_3O^+}$, s^{-1}
C_6H_5–C($SeCH_3$)=CH_2	31	5.29×10^{-3} [c]
p-$NO_2C_6H_4$–C(SeC_6H_5)=CH_2	4[b]	
C_6H_5–C(SeC_6H_5)=CH_2	32	3.43×10^{-4} [c]
CH_3–C(SeC_6H_5)=CH_2	5	1.5×10^{-3} [c]
H–C(SeC_6H_5)=CH_2	0	3.08×10^{-4} [d]
H–C($SeCH_3$)=CH_2	7.5	4.59×10^{-3} [d]

[a] Determined on the recovered vinyl selenide after ~50% conversion. [b] Hydrolysis conversion was only ~10%. [c] In 60/40 v/v dioxane/water (1 M in $HClO_4$) at 30 °C. [d] In 60/40 v/v dioxane/water (1 M in $HClO_4$) at 60 °C.

group and also that the former should be more basic than the latter. Therefore intermediate **3** is more likely to accumulate during hydrolysis of phenyl vinyl selenides than in the case of methyl vinyl selenides. Yet, reversibility is only observed for the latter. Futher support for this is provided by the observation that α-(phenylseleno)styrene incorporates about the same amount of deuterium (~32%, see below) as does α-(methylseleno)styrene (Table IV).

Selenium-Stabilized Carbonium Ions. From measurements of hydrolysis rates of phenyl vinyl ethers, sulfides, and selenides McClelland and Leung have concluded that phenoxy, phenylthio, and phenylseleno groups possess carbonium ion stabilizing properties described by a σ_P^+ parameter of value −0.62, −0.54, and −0.47, respectively.[13]

Although qualitatively in some respect, additional information to this problem can be gained from our rate and deuterium incorporation measurements. The most relevant results are summarized in Table V.

Several interesting conclusions can be drawn from these data. As was already pointed out, entries 2–4 show that even phenyl vinyl selenides can hydrolyze with a reversible protonation step, provided the intermediate carbonium ion be sufficiently stable. Thus the presence of a methyl group (entry 4) or even of a *p*-nitrophenyl group (entry 2) at the α-position of the vinyl moiety appears to stabilize the carbonium ion enough to allow the observation of some reversibility as indicated by the nonzero values of the percentages of deuterium incorporation.

On the other hand, comparison of the appropriate hydrolysis rate constants provide a quantitative measure of the stabilization of carbonium ions by α-alkyl- and/or α-arylseleno groups. Entries 1 and 3 show that α-(methylseleno)styrene hydrolyzes 15.4 times faster than α-(phenylseleno)styrene. Because of the much lower reactivity of phenyl vinyl selenide[25] rate comparison between this compound and methyl vinyl selenide had to be effected at 60 °C (entries 5 and 6). In spite of this difference, we found a rate enhancement by a factor of 14.9 in favor of methyl vinyl selenide as compared to phenyl vinyl selenide. Since essentially the same rate ratio is found for two different pairs of compounds under different conditions, we can safely consider that this factor of ~15 reflects the carbonium ion stabilizing ability of the methylseleno group as compared to that of the phenylseleno group. Together, with relative rates of hydrolysis for vinyl ethers and vinyl sulfides reported[5b] by Mc Clelland, we obtain the following series of ratios: CH_3O/C_6H_5O = 133, CH_3S/C_6H_5S = 41, and CH_3Se/C_6H_5Se = 15.

Finally, entries 3 and 4 show that 2-(phenylseleno)propene hydrolyzes 4.3 times faster than does α-(phenylseleno)styrene. A very similar observation was made by Kresge and co-workers[41] in the vinyl ether series and interpreted as arising mainly from initial-state stabilization differences.

Acknowledgment. Financial support of this work from "Fonds National de la Recherche Scientifique" (FNRS, Belgium) is gratefully acknowledged.

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(25) We could not reproduce the rate constant given for this compound in Table II of ref 13.

Chemical Consequences of a Polar Axis in a Solid–Gas Reaction. Reaction of *p*-Bromobenzoic Anhydride Crystals with Ammonia Gas. The Absolute Direction of a Polar Unitropic Reaction and the Relationship of Absolute Configuration with Crystal Morphology

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Abstract: The reaction of crystalline *p*-bromobenzoic anhydride with ammonia gas has been found to be highly anisotropic and to occur preferentially from one side; that is, a front forms which proceeds in only one direction along the polar axis. (Such a reaction is classified as a polar unitropic reaction.) The absolute direction of the polar axis has been determined by X-ray methods and correlated with the internal structure of the crystal; the preferential attack of ammonia molecules from the side of the carbonyl oxygen atoms can be explained by a mechanism in which the ammonia molecule undergoing reaction is hydrogen bonded to a carbonyl oxygen and thus correctly oriented for attack at the sp^2 carbon atom of the other carbonyl group in the same anhydride molecule. Determination of the direction of the polar axis gives at the same time the absolute configuration of the anhydride single crystal (space group *C*2), and the absolute configuration has been related to crystal morphology. It is proposed that the *RS* notation be extended to include absolute configurations of molecules such as *p*-bromobenzoic anhydride held rigidly in a chiral conformation in the crystalline state.

Although the first reactions of crystalline organic solids with gaseous reagents were described more than 100 years ago, it is only relatively recently that the improved ease of structure determination has given impetus to studies correlating chemical