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Permanganate Ion Oxidations. 16. Substituent Effects on the Rate of Oxidation of α,β-Unsaturated Carboxylate Ions[1]

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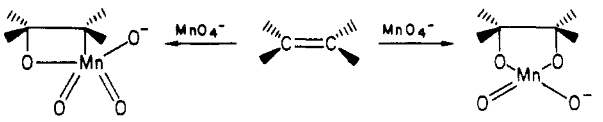
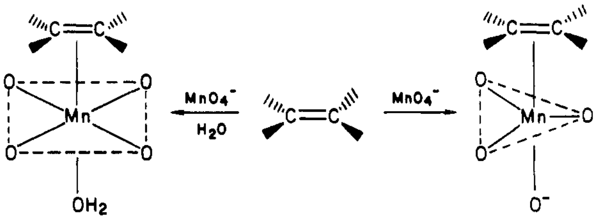
The kinetics of the permanganate ion oxidation of substituted α,β-unsaturated carboxylate ions were investigated in phosphate buffered solutions (pH 6.83 ± 0.03). Although the rate of oxidation is not very sensitive to electronic effects, steric factors appear to be important. The possible ambiphilic nature of permanganate ion is discussed. Soluble (colloidal) manganese dioxide is the inorganic product.

Although there are numerous studies of the permanganate ion oxidation of unsaturated compounds in aqueous and nonaqueous media,[1,3-33] there is a dearth of systematic data under the same experimental conditions concerning the effects of substituents on the kinetics and mechanisms of the reaction. There is also considerable uncertainty as to whether the permanganate ion oxidation of olefins involves a direct attack on the double bond by heteroatom ligands (eq 1) or an initial interaction between the double bond and the metal center to give an octahedral (**3**) or a trigonal bipyramidal (**4**) organometallic complex which can rearrange to a metallacyclooxetane (**1**) or to the long-sought elusive five-membered cyclic manganate(V) diester **2**, eq 1–3). We have investigated the kinetics of the permanganate ion oxidation of a wide variety of unsaturated carboxylate ions in order to determine whether permanganate ion is ambiphilic,[1,23] electrophilic,[27] or nucleophilic[16] and to determine the influence of substituents on the kinetics and mechanisms of the reaction.



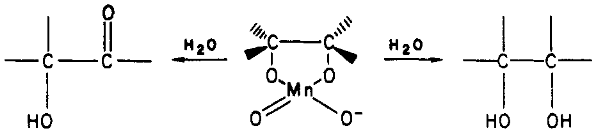
(1)

1 **2**



(2)

3 **4**



(3)

2

Experimental Section

Melting points were determined in open capillary tubes with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Robertson Laboratory, Florham Park, NJ.

IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer in CCl_4 or as neat films.

High-resolution mass spectra were obtained with a VG 7070E-HF mass spectrometer (70 eV). Medium-resolution mass spectra were obtained with a Finnigan 9610 GC-EI-CI mass spectrometer with a Nova 3 data system operating at an ionization

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potential of 70 or 100 eV. Chemical ionization mass spectra were obtained by using 2-methylpropane as the reactant gas.

^{1}H NMR spectra were recorded at 80 (Varian FT-80A) and at 250 MHz (Bruker WM-250) with the solvent(s) noted. Chemical shifts (δ) are reported downfield from internal Me_4Si (~0.5% for Fourier transform) at δ 0.00. Apparent coupling constants (J) are reported in hertz (Hz). Because of the data digitization with the FT instrument, J values are ±0.40 Hz maximum but normally are accurate to ±0.20 Hz. ^{13}C NMR data were obtained with a Bruker WM-250 spectrometer.

Solutions were prepared immediately before use in water which had been deionized and then distilled from an all-glass Corning megapure apparatus. Appropriate quantities of KH_2PO_4 and Na_2HPO_4 to maintain pH and ionic strength were dissolved in the substrate solution. Ionic strength was adjusted with KCl when necessary. The pH values were determined on an Altex ϕ60 pH meter in the substrate solution before reaction and in the product mixture after oxidation.

Phosphate buffers were dried 2 h at 110 °C and stored in a desiccator. The commercially available solid unsaturated acids were recrystallized until they gave sharp melting points, and the liquid acids were fractionally distilled under reduced pressure. The physical and spectral properties of the unsaturated acids agreed with the literature values. Propanone was distilled from anhydrous potassium carbonate and benzene from calcium hydride. Zinc dust was activated by washing with 10% HCl and then acetone and ether.[34]

2,3-Dimethyl-2-butenoic Acid (13).[35,36] Activated zinc (7.59 g, 116 mmol) was placed in a 100-mL three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a 100-mL addition funnel. The system was purged with nitrogen, and then a mixture of 30 mL of benzene, 8.06 g of propanone (92 mmol), and 16.76 g of ethyl 2-bromopropanoate (139 mmol) was syringed into the addition funnel. Approximately 5 mL of the bromo ester/propanone mixture was added to the zinc, followed by 0.5 mL of 3.0 M ethylmagnesium bromide in diethyl ether. The reaction mixture was heated to reflux, and the remainder of the bromo ester/propanone mixture was added at a rate to maintain gentle reflux.

After refluxing for 1.5 h, the contents of the flask were poured, with stirring, into 150 mL of cold 10% sulfuric acid. The benzene layer was removed and the aqueous layer extracted with 50-mL portions of benzene (3×). The combined benzene extracts were washed with 50 mL of 5% sulfuric acid, 50 mL of 10% sodium carbonate, and 50 mL of water, dried over anhydrous sodium sulfate, filtered, and distilled to azeotrope off remaining traces of water. Phosphorus pentoxide (10.42 g) was then added to the distillate and the solution refluxed for 4 h. After cooling, the benzene layer was decanted and the solid washed with 100 mL of dry benzene. The combined benzene extracts were fractionated under reduced pressure through a vacuum-jacketed distillation apparatus. The fraction collected from 105–110 °C (85 mm) gave ethyl 2,3-dimethyl-2-butenoate: ^{1}H NMR ($CDCl_3$) δ 4.18 (q, 2 H, OCH_2CH_3), 1.99 (m, 3 H), 1.80 (m, 6 H), 1.29 (t, 3 H, OCH_2CH_3).

Hydrolysis was effected by refluxing the ester for 5 h in ethanolic (25 mL) KOH (5.0 g). The product mixture was poured into 100 mL of water, extracted with ether (50 mL, 3×), rendered acidic to pH 2 with 2.0 M HCl, and again extracted with ether (50 mL, 3×). The combined acid ether extracts were dried ($MgSO_4$), and the ether was evaporated to give a mixture of 2,3-dimethyl-2-butenoic acid (**13**) and 2,3-dimethyl-3-butenoic acid. The mixture was dissolved in 10 mL of petroleum ether (30–60 °C) and cooled to −78 °C until crystals formed. The petroleum ether was decanted from the cold flask, and the flask was warmed to 22–24 °C. This freezing-out process was repeated and the solvent then evaporated at 22–24 °C to give 300 mg (3%) of 2,3-dimethyl-2-butenoic acid (**13**): mp 64.1–65.0 °C (lit.[36] mp 64–65 °C); ^{1}H NMR ($CDCl_3$) δ 2.11 (m, 3 H), 1.86 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 15.67 (C-2 CH_3) 23.55 (cis CH_3), 23.67 (trans CH_3), 121.94 (C-2), 148.34 (C-3), 175.36 (C-1); MS, m/z (relative intensity) 113 (100, molecular ion), 99 (66.33, $M^+ - CH_3$).

(*E*)-4,4-Dimethyl-2-pentenoic acid (14) was prepared according to the procedure of Sharpless and Kirshenbaum.[37] 2,2-Dimethylpropanal (1.99 g, 23.1 mmol), triphenyl(carbethoxymethylene)phosphorane[38] (10.0 g, 30.0 mmol), and 25 mL of dry THF were placed in a 50-mL round-bottomed flask. The solution was stirred at 22-24 °C for 2 days. The product mixture was filtered to remove triphenylphosphine oxide and the unreacted phosphorane. Addition of petroleum ether (30–60 °C) to the filtrate caused more precipitate to form, which was again filtered. The product ester (UV-active on TLC) was isolated by flash column chromatography (20:1 petroleum ether–ethyl ether) which gave ethyl (*E*)-4,4-dimethyl-2-pentenoate as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 6.97 (d, J = 16 Hz, 1 H), 5.72 (d, J = 16 Hz, 1 H), 4.18 (q, 2 H, OCH_2CH_3), 1.29 (t, 3 H, OCH_2CH_3), 1.08 (s, 9 H, 2-methyl-2-propyl).

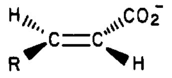
Hydrolysis was effected by stirring the ester with 10 mL of 10% KOH for 12 h. The solution was then acidified to pH 2 with 5% HCl and extracted with 25 mL of ether (3×). The organic extracts were combined, dried ($MgSO_4$), and filtered, and the solvent was evaporated to afford 400 mg (14%) of (*E*)-4,4-dimethyl-2-pentenoic acid (**14**) as a white solid: mp 60.5–61.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.08 (d, J = 16 Hz, 1 H), 5.74 (d, J = 16 Hz, 1 H), 1.09 (s, 9 H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) δ 28.79 ($C(CH_3)_3$), 34.18 ($C(CH_3)_3$), 116.52 (C-2), 162.04 (C-3), 173.22 (C-1); IR (CCl_4) 3100 (OH), 2960, 1693 (C=O), 1413, 1300, 923, 760 cm^{-1}; MS, m/z (relative intensity) 128 (20.49, molecular ion), 113 (86.03, $M^+ - CH_3$), 83 (100, $M^+ - CO_2H$).

(*E*)-2-Cyano-3-phenyl-2-propenoic Acid (20).[39] Freshly distilled phenylmethanal (5.0 g, 47.1 mmol), cyanoethanoic acid (3.94 g, 46.3 mmol), ammonium acetate (0.14 g, 1.8 mmol), and 50 mL of benzene were combined in a 100-mL round-bottomed flask attached to a Dean–Stark water separator, which in turn was attached to a reflux condenser. The mixture was heated and maintained at reflux until 0.85 mL of water was collected. The white solid was filtered from the product mixture, washed with benzene, and recrystallized from aqueous ethanol to give 5.65 g (70%) of (*E*)-2-cyano-3-phenyl-2-propenoic acid (**20**): mp 180–182 °C (lit.[40] mp 178–179 °C); ^{1}H NMR ($CDCl_3$) δ 8.32 (s, 1 H), 8.03 (m, 2 H), 7.55 (m, 3 H), 5.13 (s, 1 H, CO_2H); ^{13}C NMR (Me_2SO-d_6) δ 104.91 (C-2), 117.03 (CN), 130.24 (ortho C), 131.61 (meta C), 132.57 (para C), 134.04 (ipso C), 155.39 (C-3), 164.21 (C-1).

Rates of Reaction. The reactions were followed as previously described[1,6] by monitoring spectral changes using a Durrum Model D-110 stopped-flow spectrometer which was connected to a Tracor-Northern 1710 Multichannel Analyzer. Reaction rates were determined under pseudo-first-order conditions by measuring the disappearance of permanganate ion at 526, 584, or 660 nm and/or measuring the rate of formation of soluble (colloidal) manganese dioxide at 418 nm.[1,6] Rate constants were obtained from plots of $-\ln (A_t - A_\infty)$ or $-\ln (A_\infty - A_t)$.

Results and Discussion

Kinetics. The permanganate ion oxidation of (*E*)-2-butenoate (**5**) is first order in oxidant concentration and in substrate concentration in acid media,[16,41] in phosphate-buffered solutions,[1,9] and in alkaline solution.[9]



5, R = CH_3
6, R = C_6H_5

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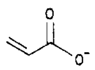
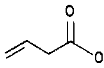
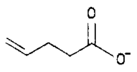
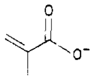
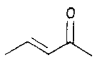
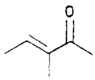
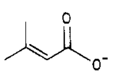
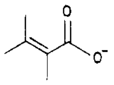
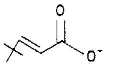
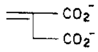
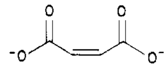
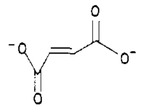
(41) The resolved rate constants for the permanganate ion oxidation of (*E*)-2-butenoic acid and (*E*)-2-butenoate at 25 °C (μ = 1.5 M) in the pH range of 0.5–5.0 are 730 and 410 M^{-1} s^{-1}, respectively.[16]

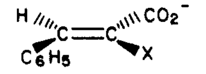
Table I. Relative Rates of the Permanganate Ion Oxidation of Aliphatic α,β-Unsaturated Carboxylate Ions[a]

compd	carboxylate ion	k,[b] $M^{-1}\,s^{-1}$	k_{rel}[c]	k_{rel}[j]
7		442 ± 1	1.00	
8[d]		127	0.29	
9[e]		178 ± 1	0.40	
10		450 ± 2	1.02	
5[f]		286 ± 1	0.65	
11[g]		569 ± 1	1.29	
12		57 ± 1	0.13	
13[h]		34 ± 1	0.08	
14[i]		105 ± 1	0.24	
15		216 ± 1	0.49	1.00
16		258 ± 3	0.58	1.19
17		633	1.43	2.93

[a] Temperature = 25.0 °C; [carboxylate ion] = 4.00 × 10^{-3} M; [MnO_4^-] = 4.00 × 10^{-4} M; [KH_2PO_4] = [Na_2HPO_4] = 0.20 M; pH = 6.83 ± 0.03; μ = 0.80. [b] Second-order rate constant = $k = k_\psi/$[carboxylate ion]. [c] Relative to 2-propenoate (7). [d] Rate for formation of soluble (colloidal) manganese dioxide at 418 nm = 139 ± 2 $M^{-1}\,s^{-1}$. [e] At 418 nm, k = 187 ± 1 $M^{-1}\,s^{-1}$. [f] At 418 nm, k = 279 ± 1 $M^{-1}\,s^{-1}$. [g] At 418 nm, k = 585 ± 10 $M^{-1}\,s^{-1}$. [h] At 418 nm, k = 37 ± 1 $M^{-1}\,s^{-1}$. [i] At 418 nm, k = 116 ± 2 $M^{-1}\,s^{-1}$. [j] Relative to 2-methylidene-1,4-butanedioate (15).

Second-order kinetics have also been obtained for the permanganate ion oxidation of (*E*)-3-phenyl-2-propenoate (**6**) in acid,[19b,21] in neutral,[1] and in alkaline solutions.[24a] The kinetics of the permanganate ion oxidation of α,β-unsaturated carboxylate ions **5** and **7-14**, and dicarboxylate ions **15–17** were determined in phosphate buffered solution (Table I).

The rate of permanganate ion oxidation of substituted 2-propenoates **6** and **18–20** were also determined for comparison purposes.



	X	k, $M^{-1}\,s^{-1}$	k_{rel}
6	H	691 ± 1	1.00
18	CH_3	271 ± 3	0.39
19	C_6H_5	28 ± 1	0.04
20	CN	1134 ± 8	1.64

Relative Rates: Terminal unsubstituted unsaturated carboxylates **7–9** are oxidized at similar rates in phosphate buffered solutions (pH 6.86) regardless of the center of unsaturation relative to the carboxylate ion (Table I), which may suggest only a small interaction between the carboxylate anion and the carbon–carbon double bond.

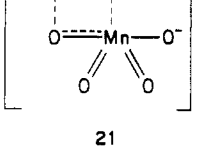
Although substitution of a methyl group for hydrogen at the α-position of **7** (to give **10**) has no influence on the rate, substitution of a methyl group for hydrogen at the α-position of **5** (to give **11**) doubles the rate of oxidation relative to **5**. Methyl substitution (trans) at the β-position of **7** (to give **5**) slows the rate 0.65 and β-methyl substitution on **12** (to give **13**) slows the rate 0.12 relative to **7**. These relative rate data are not consistent with an electrophilic attack by permanganate ion at the carbon–carbon double bond since increasing the nucleophilicity (increasing the number of methyl groups) of the double bond generally accelerates the rate of electrophilic addition.[42,43]

From the relative rates in Table I one can see that replacing a hydrogen in **7** with a trans methyl (to give **5**) or trans (2-methyl-2-propyl) (to give sterically encumbered **14**) slows the rate. Similarly, increasing steric bulk slows the rate of oxidation of **18** and **19** relative to **6**. Thus, steric factors influence the rate of oxidation. The relatively slow rate of oxidation of 2,3-dimethyl-2-butenoate (**13**) is also attributable to steric hindrance.

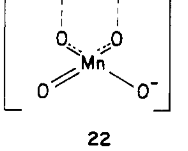
The greater reactivity of (*E*)-2-butenedioate (**17**) relative to (*Z*)-2-butenedioate (**16**) is probably due to steric effects in the activated complex of **16** as the sp^2-hybridized carbon atoms (bond angles ca. 120°) approach sp^3 hybridization (bond angles ca. 109.5°) and to electronic repulsion between eclipsing cis carboxylate ions.[14] Unfavorable eclipsing interactions may also contribute to the lower reactivity of **5**, **12**, **13**, and **15** relative to **7**.

Although the double bond of (*E*)-2-butenedioate (**17**) may be more electron deficient than the double bond in 2-propenoate (**7**), it is oxidized at a faster rate. This may suggest nucleophilic character for permanganate ion.[8,9,16] Similarly, (*E*)-2-cyano-3-phenyl-2-propenoate (**20**) reacts slightly faster than **6**. Contrary to steric considerations, (*E*)-3-phenyl-2-propenoate (**6**), which may exhibit conjugative electron withdrawal, reacts faster than (*E*)-3-methyl-2-propenoate (**5**).

The low sensitivity of permanganate ion to electronic effects, the small ρ values for the oxidation of **6**,[1,9,21,22] the inverse secondary kinetic deuterium isotope effects,[21-23,44] the ^{18}O studies,[8] the low enthalpy of activation, and the relatively large negative entropy of activation combine to suggest that permanganate ion undergoes cycloaddition with the carbon-carbon double bond to yield metallacyclooxetane **1** via **21** or cyclic manganate(V) diester **2** via **22** in the rate-determining step (eq 1).[45-48]



21



22

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(42) Freeman, F. *Chem. Rev.* **1975**, *75*, 439.

(43) It is of interest to note that permanganate ion oxidizes 5-methyluracil 194 times faster than 6-methyluracil.[6,7]

(44) Freeman, F.; Chang, L. Y., unpublished data.

(45) Littler, J. S. *Tetrahedron* **1971**, *27*, 81.

(46) (a) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 448. (b) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287.

(47) The remarkable similarity between cycloaddition reactions and the permanganate ion oxidation of carbon–carbon double bonds has been suggested by Wiberg and Geer.[9]

(48) Sharpless and co-workers[27] have questioned why the electron-rich oxygen atoms in oxo transition metals should make an electrophilic attack on a carbon–carbon double bond to afford **22**.

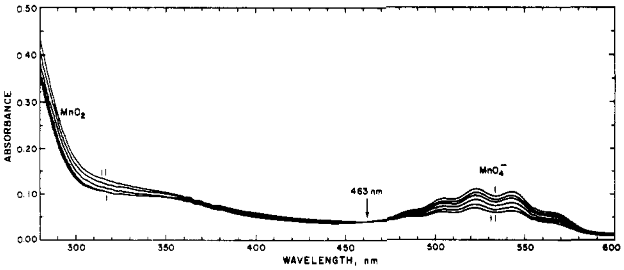

Figure 1. Successive ultraviolet–visible spectra (overall 11 scans; chart speed 10 nm s^{-1}) for disappearance of permanganate ion (4.00×10^{-5} M) and formation of manganese dioxide during the oxidation of 2,3-dimethyl-2-butenoate (**13**, 4.00×10^{-5} M) in 0.20 M KH_2PO_4–Na_2HPO_4 (pH 6.83, $\mu = 0.80$, isosbestic point 463 nm). The reference cell contained 0.20 M buffers.

Reduction of Manganese. A typical ultraviolet–visible change for the permanganate ion oxidation of α,β-unsaturated carboxylate ions is shown in Figure 1. Corresponding to the disappearance of the permanganate ion peak at 526 nm is the appearance of the characteristic spectrum of manganese dioxide. Excellent isosbestic points in the 465-nm region suggest a reaction with no buildup of an intermediate. Spectrophotometric and titritmetric analyses have shown this manganese species to be of oxidation state 4 (MnO_2).[1,6-8,19b,22,23]

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Registry No. **5**, 13095-94-8; **6**, 17263-38-6; **7**, 10344-93-1; **8**, 54467-93-5; **9**, 20224-66-2; **10**, 18358-13-9; **11**, 19342-43-9; **12**, 18358-40-2; **13**, 101225-65-4; **13** (protonated acid), 4411-97-6; **14**, 101225-66-5; **14** (protonated acid), 16666-45-8; **15**, 2964-00-3; **16**, 142-44-9; **17**, 142-42-7; **18**, 66482-37-9; **19**, 101225-67-6; **20**, 101225-68-7; **20** (protonated acid), 14378-06-4; $CH_3CHBrCO_2Et$, 535-11-5; CH_3COCH_3, 67-64-1; *t*-BuCHO, 630-19-3; $Ph_3P{=}CHCO_2Et$, 1099-45-2; (E)-*t*-BuCH=$CHCO_2Et$, 87995-20-8; PhCHO, 100-52-7; $CNCH_2CO_2H$, 372-09-8; MnO_4^-, 14333-13-2; etyhl 2,3-dimethyl-2-butenoate, 13979-28-7.

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^{77}Se NMR. 2.[1] The Basis for Application of J_{Se-Se} and J_{Se-H} in Structure Assignments of Mono-, Di-, and Triseleno-Substituted Alkenes

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Series of isomeric mono-, di-, and triseleno-substituted alkenes have been synthesized and subjected to ^{77}Se NMR analysis. In di- and triseleno-substituted alkenes stereochemical assignments were obtained by measurements of ^{77}Se–^{77}Se coupling constants. Values between 117–77 Hz for cis $^3J_{Se-Se}$, 55–19 Hz for $^2J_{Se-Se}$, and 12–2 Hz for trans $^3J_{Se-Se}$ were found. A large body of vinylic ^{77}Se–^{1}H coupling constants has been obtained in di- and trisubstituted ethenes. This parameter also shows a stereochemical dependence, i.e., trans $^3J_{Se-H} \sim 1$–4 Hz, cis $^3J_{Se-H} \sim 6$–10 Hz, and $^2J_{Se-H} \sim 11$–26 Hz. The stereochemistry of the base-catalyzed reaction of 1-alkynes with diselenides and the addition of benzeneselenol to alkynyl selenides are discussed in terms of the ^{77}Se NMR based structural assignments.

Introduction

In the field of synthetic organic chemistry, organoselenium compounds including alkenyl selenides have proved to be valuable synthetic precursors.[2,3]

In order to utilize selenium compounds as synthons, it is of major importance to have efficient analytical methods available. Standard spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR, MS) provide some information about the structure of these compounds, but in particular the identification of structural isomers causes severe problems. This is especially a problem within the synthetically important group of alkenylic selenides. Apart from cases where the presence of a vinylic proton–proton coupling constant can reveal the stereochemistry, no methods of general applicability are available for isomer assignments in selenium-substituted alkenes.

Several features make ^{77}Se NMR the ideal tool for solving the above mentioned problems. The relatively high receptivity of the ^{77}Se spin $^1/_2$ nucleus (three times better than ^{13}C)[4] allows easy measurements even on low-field instruments of not only chemical-shift values but also ^{1}H–^{77}Se coupling constants. The large spread in shielding of ^{77}Se ($\sim$3000 ppm) combined with narrow lines ($\Delta\nu_{1/2} \lesssim 1$ Hz normally) result in well-resolved lines and coupling patterns even when mixtures of several configurational isomers are studied. Moreover, if the molecule contains two or more nonequivalent selenium atoms, ^{77}Se–^{77}Se coupling constants can be measured. This very useful parameter is obtainable from the selenium satellites in the proton-noise-decoupled ^{77}Se NMR spectra. However, ^{77}Se NMR can not be applied efficiently in structure elucidation due to the lack of a sufficient body of relations between ^{77}Se NMR parameters and molecular structure.

In a previous paper[1] we established a relationship between the vicinal coupling constant $^3J_{Se-Se}$ and the cis/trans orientation of the selenium atoms in selenium-substituted alkenes. These promising results have led us to undertake a systematic ^{77}Se NMR study of selenium-substituted alkenylic systems. Within this group of com-

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[1] Johannsen, I.; Eggert, H. *J. Am. Chem. Soc.* **1984**, *106*, 1240.

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