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Notes

The Styrene Probe in Substituent-Induced Chemical Shifts: ^{77}Se and ^{13}C NMR Spectra of Ethyl α-(Phenylseleno)cinnamates

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Introduction

The NMR spectra of compounds containing the styrene skeleton have been used extensively for the quantitative evaluation of the transmission of substituent effects through an extended π system because side-chain atoms are far enough removed to minimize anisotropic effects of substituents.[2] The π polarization mechanism is the predominant effect in determining the distribution of electron density at side-chain sites. The substituent polarizes the π system in the side chain such that there occurs a regular alternation of increased and decreased charge densities as compared to those in the unsubstituted parent, and this effect also continues in more extensively conjugated systems.[3] Although many series of styrenes bearing substituents on side-chain atoms have been investigated, β-substituents have almost invariably been electron withdrawing by both inductive and mesomeric effects.[3-5]

The ^{13}C spectra of styrenes in which the cyano group is present as a β-substituent show the expected inverse substituent effects at the cyano carbon, as do the ^{31}P spectra in which the phosphorus atom is present as a β-(diethylphosphono) substituent.[5] The ^{19}F NMR spectra of β-flouro-β-carbethoxystyrenes (ethyl α-fluorocinnamates), on the other hand, reveal unexpected, normal substituent effects.[6] Of the β-substituents studied to date, the fluorine atom is unique in that it belongs to the same period as carbon and serves as a strong, mesomerically electron-donating substituent, in opposition to its inductive electron withdrawal. Consequently, it was of interest to extend the styrene studies to series containing other β-substituents capable of electron donation. Toward this end, the selenium atom seemed of interest.

The ^{77}Se nucleus is particularly well suited for evaluating electronic effects. Its wide chemical shift range and its remarkable sensitivity to small changes in the electronic structure of the selenium atom have been noted[7] and earlier NMR studies have been reviewed;[8] however, there is no report of the styrene probe having been applied to ^{77}Se NMR. Accordingly, we have investigated the ^{77}Se and the ^{13}C spectra of the *E* and *Z* isomers of a series of ethyl 2-(phenylseleno)-3-(4-R-phenyl)-2-propenoates (ethyl α-(phenylseleno)cinnamates).

Experimental Section

Ethyl (*E* + *Z*)-2-(phenylseleno)-3-(3- or 4-R-phenyl)-2-propenoates (ethyl α-(phenylseleno)cinnamates) were prepared by an adaptation of the method used by Lehnert[9] for the synthesis of ethyl α-(diethylphosphono)cinnamates, as depicted in Scheme I. The numbering system used in reporting the chemical shifts, the substituents used, and the series designations are also shown in Scheme I.

Dry tetrahydrofuran, 80 mL, distilled from the blue sodium ketyl of benzophenone, was placed under a nitrogen purge in a 250-mL three-necked flask equipped with magnetic stir bar, N_2 inlet, and thermometer adapter. Under a nitrogen blanket, the internal temperature was lowered to 0 °C using an ice–salt bath. A solution of $TiCl_4$ (5 mL, ACS purified) and spectral-grade carbon tetrachloride (10 mL) was added dropwise over a 30-min period, and the temperature was kept below 5 °C during the addition. A solution of ethyl (phenylseleno)acetate (9.86 g, 0.02 mol) and *p*-tolualdehyde (2.4 g, 0.02 mol), or other appropriate aldehyde, in 20 mL of dry THF was added in one portion through the addition funnel to the THF/$TiCl_4$ suspension.

Finally, 9.0 mL of dry *N*-methylmorpholine (distilled under N_2 from CaH_2) was added over a 10-min period to the reaction mixture, and stirring was continued for 3 h (at <5 °C). The mixture was allowed to warm to room temperature overnight, and 20 mL of water was added with stirring to dissolve the hydrochloride salts. The aqueous phase was separated and extracted with three 50-mL portions of ether; the organic layers were combined, washed with saturated $NaHSO_3$, and dried over $MgSO_4$. After removal of the ether, those products having the more polar substituents on the ring (*p*-CO_2Me, *p*-CN, *m*-CN, and *m*- but not *p*-NO_2) became crystalline after standing either on the bench or in the cold room. Suction filtration, washing with cold hexanes (to remove excess ethyl (phenylseleno)acetate), and recrystallization (petroleum ether or petroleum ether/CH_2Cl_2) gave exclusively the *E* isomers in low overall yield (7–17%).

In other cases, crystalline product separated after solvent removal from chromatography fractions (*p*-Cl, *m*-Cl, *p*-CF_3, *m*-CF_3, and *p*-Ph). In some of these cases, both *E* and *Z* isomers were present. Those compounds with less polar substituents remained as oils. Vacuum distillation to remove excess ethyl (phenylseleno)acetate followed by silica gel chromatography provided the product as an *E*/*Z* isomer mixture. Early chromatographic fractions were relatively enriched in the less abundant *Z* isomer; however, a quantitative separation was never obtained by chromatography. Since these isomers could be

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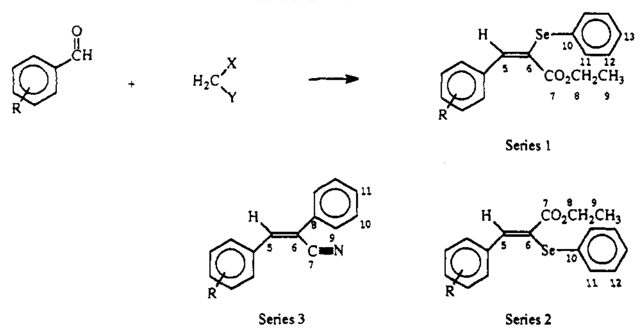
Scheme I



R

a = p-NMe$_2$
b = p-OMe
c = p-Me
d = p-Ph
e = p-F
f = H
g = m-OMe*
h = p-Cl
i = m-F
j = m-Cl*
k = m-CF$_3$
l = p-CO$_2$Me*
m = p-CF$_3$
n = m-CN*
o = m-NO$_2$*
p = p-CN*
q = p-NO$_2$

* Not isolated in Series 2.

differentiated based on their coupling constants, further attempts at separation were not made.

The *p*-nitro derivative was formed in much lower yield than any other in this series (3.18%) and was the only one in which the *Z* isomer was greatly predominant. It was prepared at a lower temperature (−78 °C) and never became crystalline as did the other compounds with polar substituents.

Chromatography purification was accomplished on a 200-g silica gel column (70–230 mesh) slurry-packed in hexanes. The eluant consisted of hexanes (1 L) followed by increased concentrations of ethyl acetate in 1% increments (per 500 mL of eluant volume) up to 6% ethyl acetate. Isomer ratios, series 1/series 2, were obtained from the total ion currents in the mass spectra. Gas chromatography/mass spectrometry was performed with a Hewlett-Packard 5890 GC/5970A mass selective detector. Infrared spectra were recorded on neat liquids using NaCl plates (solids were obtained as melts) by means of a Mattson Polaris FTIR (Nu 10000) spectrophotometer. Values are given in cm^{-1}. All NMR spectra were obtained with a VXR-400 instrument (Varian Associates). ^{77}Se, ^{13}C, and ^{1}H spectra were recorded at 76.295, 100.573, and 399.928 MHz, respectively. Samples (0.3 g each) were dissolved in 2.5 mL of CDCl$_3$. For the ^{77}Se spectra chemical shifts were measured relative to external dimethyl selenide which was placed in a 3-mm diameter capillary inside a 10-mm diameter NMR tube. ^{13}C spectra are reported relative to the center CDCl$_3$ peak at 77 ppm, and ^{1}H spectra are reported downfield from (initial) TMS. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN, or by Desert Analytics, Inc., Tucson, AZ.

Seventeen compounds were made, 11 of which were composed of both the *E* and *Z* isomers. In all cases, except the *p*-OMe and *p*-NO$_2$ derivatives, the *E* compound was either more prevalent or the only isomer. These isomers were differentiated by selective decoupling of the Se–aromatic hydrogens and evaluation of the Se–vinylic hydrogen coupling constant. For the *E* isomer, 6–8-Hz coupling constants were observed, and for the *Z* isomer 4–5-Hz *J* values. Johannson, Henriksen, and Eggert[11] have reported *J* values of 6–10 and 1–4 Hz, respectively, for the cis and the trans coupling constants.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-[4-(dimethylamino)phenyl]-2-propenoate (1a + 2a): yellow-green oil; 3.9% yield; *E*/*Z* ratio = 1.10; IR 694, 730, 812, 1187, 1699; MS *m*/*e* (relative intensities) 377 (10.6, M$^+$ + 2), 375 (49.6, M$^+$), 373 (29.2, M$^+$ − 2), 330, 302, 295, 223, 144 (100); ^{1}H NMR δ 1.08 (t, 3 H, *J* = 7.12 Hz), 2.99 (s, 6 H) 4.10 (q, 2 H, *J* = 7.11 Hz), 8.23 (s, 1 H), 6.59–7.82 (m, 9 H). Anal. Calcd: Se, 21.09. Found: Se, 20.61.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(4-methoxyphenyl)-2-propenoate (1b + 2b): yellow oil; 25.8% yield; *E*/*Z* ratio = 0.99; IR 687, 749, 832, 1182, 1710; MS *m*/*e* (relative intensities) 364 (7.6, M$^+$ + 2), 362 (37.4, M$^+$), 360 (19.4, M$^+$ − 2), 289, 208, 165 (100); ^{1}H NMR δ 1.06 (t, 3 H, *J* = 7.11 Hz), 3.82 (s, 3 H), 4.08 (q, 2 H, *J* = 7.14 Hz), 8.17 (s, 1 H), 6.81–7.74 (m, 9 H). Anal. Calcd: Se, 21.85. Found: Se, 21.03.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(4-methylphenyl)-2-propenoate (1c + 2c): yellow oil; 58.3% yield; *E*/*Z* ratio = 4.08; IR 700, 747, 777, 1195, 1713; MS *m*/*e* (relative intensities) 348 (8.5, M$^+$ + 2), 346 (40.9, M$^+$), 344 (20.9, M$^+$ − 2), 273, 192, 149, 115 (100); ^{1}H NMR δ 1.03 (t, 3 H, *J* = 7.11 Hz), 2.36 (s, 3 H), 4.05 (q, 2 H, *J* = 7.14 Hz), 8.19 (s, 1 H), 7.18–7.60 (m, 9 H). Anal. Calcd: C, 62.61; H, 5.25; Se, 22.87. Found: C, 63.16; H, 5.29; Se, 22.62.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(4-phenylphenyl)-2-propenoate (1d + 2d): amorphous waxy solid; mp 39–45 °C; 27.7% yield; *E*/*Z* ratio = 16.95; IR 690, 700, 743, 830, 1190, 1713; MS *m*/*e* (relative intensities) 410 (8.1, M$^+$ + 2), 408 (42.2, M$^+$), 406 (17.8, M$^+$ − 2), 334, 254, 178 (100); ^{1}H NMR δ 1.05 (t, 3 H, *J* = 7.10 Hz), 4.07 (q, 2 H, *J* = 7.14 Hz), 8.19 (s, 1 H), 7.19–7.76 (m, 14 H).

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(4-fluorophenyl)-2-propenoate (1e + 2e): yellow oil; bp = 157–159 °C/0.20 Torr; 36.0% yield; *E*/*Z* ratio = 6.99; IR 683, 740, 827, 1195, 1710; MS *m*/*e* (relative intensities) 352 (12.3, M$^+$ + 2), 350 (61.8, M$^+$), 348 (31.3, M$^+$ − 2), 305, 277, 196, 153 (100); ^{1}H NMR δ 1.06 (t, 3 H, *J* = 7.08 Hz), 4.08 (q, 2 H, *J* = 7.08 Hz), 8.19 (s, 1 H), 7.05–7.69 (m, 9 H). Anal. Calcd: Se, 22.60. Found: Se, 22.79.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-phenyl-2-propenoate (1f + 2f): yellow oil (lit.[10] reports that the pure *E* isomer mp = 37.5–40.0 °C); 28.8% yield; *E*/*Z* ratio = 6.13; IR 680, 733, 1202, 1705; MS *m*/*e* (relative intensities): 334 (9.4, M$^+$ + 2), 332 (49.4, M$^+$), 330 (26.1, M$^+$ − 2), 157 (100); ^{1}H NMR δ 1.03 (t, 3 H, *J* = 7.08 Hz), 4.06 (q, 2 H, *J* = 7.08 Hz), 8.15 (s, 1 H), 7.18–7.65 (m, 10 H).

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(3-methoxyphenyl)-2-propenoate (1g + 2g): yellow oil; 25.3% yield; *E*/*Z* ratio = 3.13; IR 694, 737, 780, 1167, 1717; MS *m*/*e* (relative intensities) 364 (3.7, M$^+$ + 2), 362 (18.6, M$^+$), 360 (9.4, M$^+$ − 2), 289, 208 (100); ^{1}H NMR δ 1.04 (t, 3 H, *J* = 7.11 Hz), 3.79 (s, 3 H), 4.06 (q, 2 H, *J* = 7.11 Hz), 8.11 (s, 1 H), 6.91–7.41 (m, 9 H).

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(4-chlorophenyl)-2-propenoate (1h + 2h): light yellow solid, mp = 32–36 °C; 20.5% yield; *E*/*Z* ratio = 3.13; IR 687, 737, 823, 1198, 1717; MS *m*/*e* (relative intensities) 368 (43.4, M$^+$ + 2), 366 (99.3, M$^+$), 364 (50.0, M$^+$ − 2), 291, 258, 212, 169 (100); ^{1}H NMR δ 1.05 (t, 3 H, *J* = 7.13 Hz), 4.07 (q, 2 H, *J* = 7.13 Hz), 8.07 (s, 1 H), 7.20–7.60 (m, 9 H). Anal. Calcd: Se, 21.59. Found: Se, 21.36.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(3-fluorophenyl)-2-propenoate (1i + 2i): yellow oil; 19.5% yield; *E*/*Z* ratio = 250; IR 680, 733, 767, 1180, 1713; MS *m*/*e* (relative intensities) 352 (9.4, M$^+$ + 2), 350 (48.2, M$^+$), 348 (25.3, M$^+$ − 2), 303, 277, 196 (100), 157; ^{1}H NMR δ 1.05 (t, 3 H, *J* = 7.14 Hz), 4.07 (q, 2 H, *J* = 7.11 Hz), 8.05 (s, 1 H), 6.93–7.64 (m, 9 H).

(*E*)-Ethyl 2-(phenylseleno)-3-(3-chlorophenyl)-2-propenoate (1j): light yellow solid; mp = 56–58 °C; 34.5% yield; *E* isomer only; IR 687, 740, 783, 1197, 1698; MS *m*/*e* (relative intensities) 368 (38.9, M$^+$ + 2), 366 (76.1, M$^+$), 364 (43.6, M$^+$ − 2), 321, 292, 258, 212, 157 (100); ^{1}H NMR δ 1.06 (t, 3 H, *J* = 7.13 Hz), 4.07 (q, 2 H, *J* = 7.13 Hz), 8.02 (s, 1 H), 7.19–7.63 (m, 9 H).

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-[3-(trifluoromethyl)phenyl]-2-propenoate (1k + 2k): light yellow solid; mp = 53–54.5 °C, 17.5% yield; *E*/*Z* ratio = 3.47; IR: 699, 740, 800, 1200, 1703; MS *m*/*e* (relative intensities) 402 (15.6, M$^+$ + 2), 400 (71.9, M$^+$), 398 (36.3, M$^+$ − 2), 355, 326, 246, 157 (100); ^{1}H NMR δ 1.08 (t, 3 H, *J* = 7.14 Hz), 4.10 (q, 2 H, *J* = 7.11 Hz), 8.10 (s, 1 H), 7.18–7.86 (m, 9 H). Anal. Calcd: C, 54.15; H, 3.79; F, 14.27; Se, 19.78. Found: C, 54.35; H, 3.64; F, 13.93; Se, 20.13.

(*E*)-Ethyl 2-(phenylseleno)-3-(4-carbomethoxyphenyl)-2-propenoate (1l): bright yellow solid; mp 55–56 °C; 7.7% yield; *E* isomer only; IR 698, 740, 780, 1198, 1713, 1730; MS *m*/*e* (relative intensities) 392 (11.9, M$^+$ + 2), 390 (65.0, M$^+$), 388 (32.9, M$^+$ − 2), 359, 345, 316, 285, 258, 236, 193 (100), 157; ^{1}H NMR δ 1.05 (t, 3 H, *J* = 7.10 Hz), 3.91 (s, 3 H), 4.06 (2 H, *J* = 7.12 Hz), 8.09 (s, 1 H), 7.19–8.05 (m, 9 H). Anal. Calcd: Se, 20.28. Found: Se, 20.47.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-[4-(trifluoromethyl)phenyl]-2-propenoate (1m + 2m): light yellow solid; mp =

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[11] Johannson, I.; Henriksen, L.; Eggert, H. *J. Org. Chem.* 1986, *51*, 1657–1663.

Table I. ^{13}C Assignments for Series 1

	carbon atom no.								
compd	5	6	7	8	9	10	11	12	13
1a	147.62	111.70	167.28	61.42	13.79	129.61	130.39	128.94	126.27
1b	145.58	120.47	166.78	61.66	13.77	129.61	131.09	129.01	126.75
1c	145.27	128.17	166.63	61.69	13.75	129.18	131.45	128.99	126.89
1d	144.46	131.00	166.55	61.78	13.76	129.26	131.64	129.04	127.00
1e	143.78	131.15	166.46	61.85	13.77	129.31	131.56	129.08	127.09
1f	144.78	130.92	166.51	61.76	13.73	129.24	131.66	129.00	127.01
1g	144.49	131.64	166.53	61.79	13.75	129.27	131.71	129.02	127.05
1h	143.28	133.44	166.32	61.88	13.75	129.34	131.73	129.08	127.19
1i	142.73	135.59	166.28	61.91	13.73	129.36	131.95	129.08	127.26
1j	142.45	136.75	166.20	61.91	13.74	129.31	132.01	129.06	127.27
1k	142.21	135.80	166.18	62.02	13.76	129.46	132.11	129.11	127.37
1l	142.61	139.43	166.18	61.92	13.70	129.27	132.07	129.06	127.33
1m	142.15	138.62	166.16	62.04	13.75	129.48	132.20	129.14	127.45
1n	140.98	136.27	165.94	62.12	13.80	129.78	132.20	129.21	127.54
1o	140.64	136.56	165.93	62.14	13.78	129.61	132.28	129.13	127.55
1p	141.06	139.46	165.91	62.09	13.72	129.75	132.22	129.14	127.56
1q	140.57	141.51	165.99	62.27	13.76	129.27	132.48	129.27	127.77

33–35 °C; 6.1% yield; *E*/*Z* ratio = 5.92; IR 694, 740, 827, 1200, 1720; MS *m*/*e* (relative intensities) 402 (15.6, $M^+ + 2$), 400 (71.9, M^+), 398 (36.3, $M^+ - 2$), 355, 326, 246, 157 (100); ^{1}H NMR δ 1.06 (t, 3 H, *J* = 7.08 Hz), 4.08 (q, 2 H, *J* = 7.11 Hz), 8.09 (s, 1 H), 7.20–7.69 (m, 9 H).

(*E*)-Ethyl 2-(phenylseleno)-3-(3-cyanophenyl)-2-propenoate (1n): yellow-green solid; mp = 106–107 °C; 13.3% yield; *E* isomer only; IR 690, 740, 796, 1170, 1698, 2227; MS *m*/*e* (relative intensities) 359 (12.7, $M^+ + 2$), 357 (72.7, M^+), 355 (34.8, $M^+ - 2$), 312, 284, 203, 157 (100); ^{1}H NMR δ 1.09 (t, 3 H, *J* = 7.07 Hz), 4.11 (q, 2 H, *J* = 7.08 Hz), 8.03 (s, 1 H), 7.35–7.87 (m, 9 H).

(*E*)-Ethyl 2-(phenylseleno)-3-(3-nitrophenyl)-2-propenoate (1o): light yellow solid; mp = 80–81 °C; 17% yield; *E* isomer only; IR 674, 735, 802, 1202, 1530, 1710; MS *m*/*e* (relative intensities) 379 (19.6, $M^+ + 2$), 377 (100.0, M^+), 375 (49.7, $M^+ - 2$), 332, 303, 286, 258, 157; ^{1}H NMR δ 1.12 (t, 3 H, *J* = 7.16 Hz), 4.13 (q, 2 H, *J* = 7.16 Hz), 8.46 (s, 1 H), 7.17–8.16 (m, 9 H). Anal. Calcd: Se, 20.98. Found: Se, 20.55.

(*E*)-Ethyl 2-(phenylseleno)-3-(4-cyanophenyl)-2-propenoate (1p): yellow-green solid; mp = 110–111 °C; 17.8% yield; *E* isomer only; IR 690, 743, 827, 1200, 1710, 2214; MS *m*/*e* (relative intensities) 359 (12.7, $M^+ + 2$), 357 (72.7, M^+), 355 (34.8, $M^+ - 2$), 312, 284, 203, 157 (100); ^{1}H NMR δ 1.07 (t, 3 H, *J* = 7.08 Hz), 4.08 (q, 2 H, *J* = 7.10 Hz), 8.03 (s, 1 H), 7.20–7.67 (m, 9 H). Anal. Calcd: C, 60.68; H, 4.24; Se, 22.16. Found: C, 60.51; H, 4.16; Se, 21.46.

(*E* + *Z*)-Ethyl 2-(phenylseleno)-3-(4-nitrophenyl)-2-propenoate (1q + 2q): yellow-orange oil; 3.18% yield; *E*/*Z* ratio = 0.15; IR 687, 733, 853, 1198, 1515, 1720; MS *m*/*e* (relative intensities) 379 (13.7, $M^+ + 2$), 377 (73.7, M^+), 375 (37.0, $M^+ - 2$), 332, 331, 303, 258, 227, 157 (100); ^{1}H NMR δ 1.08 (t, 3 H, *J* = 7.18 Hz), 4.09 (q, 2 H, *J* = 7.09 Hz), 8.06 (s, 1 H), 7.21–8.22 (m, 9 H).

Correlations

Single Substituent Analysis. Series 1 (*E* Isomer). ^{13}C chemical shifts of C5-C13 for 17 members of series 1 are given in Table I. Table II shows σ^{13} values and ^{77}Se chemical shifts for both series 1 and series 2. The σ^{13} values for the *p*-CO_2Me and the *m*- and *p*-CF_3 substituents have been determined in the usual manner[3] and included in this list. Other substituent constants for both single and dual parameter analysis were the same as those used in ref 4. ^{13}C chemical shifts of C8–C11 for (the same 17 members of) series 3 ((*Z*)-α-phenylcinnamonitriles) are given in Table III for comparison with the phenylseleno derivatives. Table IV contains a summary of the single-substituent parameter correlations for the ^{13}C and ^{77}Se analyses from series 1–3. Both the coefficient of determination, R^2, and the ρ-value from each correlation are given.

Table II. ^{77}Se Assignments in Series 1 and 2

		series		
substitnt	σ^{13}	1 (*E* isomer)	2 (*Z* isomer)	$\Delta\delta$ (*Z*–*E*)
a	−1.75	326.83	472.71	145.88
b	−0.74	338.80	475.16	136.36
c	−0.30	347.50	475.38	127.88
d	−0.10	351.41	478.07	126.66
e	−0.05	346.60	476.59	129.99
f	0.00	351.80	475.92	124.12
g	0.05	355.10		
h	0.13	351.30	478.41	127.11
i	0.35	356.75	478.43	121.68
j	0.36	356.92		
k	0.52	356.00	478.34	122.34
l	0.53	361.40		
m	0.66	360.06	479.90	119.84
n	0.69	358.46		
o	0.79	359.03		
p	0.85	364.50		
q	1.01	367.45	485.38	117.93

Table III. ^{13}C Assignments for Series 3 α-Phenylcinnamonitriles

	atom			
compd	8	9	10	11
3a	135.50	125.32	128.80	127.84
3b	134.76	125.68	128.94	128.66
3c	134.69	125.88	128.98	128.98
3d	134.55	125.97	129.08	128.94
3e	134.26	125.92	129.08	129.25
3f	134.46	125.96	129.03	129.15
3g	134.31	125.91	129.00	129.14
3h	134.07	125.92	129.06	129.35
3i	134.03	126.07	129.14	129.56
3j	133.90	126.03	129.11	129.56
3k	133.82	126.12	129.23	129.59
3l	133.91	126.09	129.12	129.68
3m	133.79	126.17	129.25	129.89
3n	133.50	126.13	129.25	129.97
3o	133.46	126.19	129.28	130.09
3p	133.59	126.25	129.29	130.12
3q	133.49	126.27	129.29	130.26

Several conclusions can be drawn from the tables. First, only the β carbon, C-6, of the styrene side chain shows high sensitivity to substituent effects (ρ = 10–18 in the various correlations), and the R^2 values for these correlations, although satisfactory, are well below those for similar correlations in many other series, where they are typically >0.99. It should be noted, however, that the present values apply to single analyses that include both meta and para substituents and that R^2 values are frequently significantly improved if the two types of

Table IV. Correlation Results for Series 1–3

	R^2 (slope) for Hammett scales			
	σ^{13}	σ^+	σ	σ^-
Series 1 (*E* isomer)				
C-4	0.861 (6.21)	0.839 (6.54)	0.810 (9.84)	0.839 (8.38)
C-5	0.909 (–2.78)	0.876 (–2.91)	0.966 (–4.67)	0.911 (–3.80)
C-6	0.959 (10.80)	0.961 (11.54)	0.911 (17.19)	0.873 (14.10)
C-7	0.959 (–0.52)	0.937 (–0.54)	0.973 (–0.85)	0.892 (–0.68)
C-8	0.909 (0.29)	0.867 (0.31)	0.952 (0.49)	0.933 (0.41)
C-9	0.101 (–0.01)	0.114 (–0.01)	0.064 (–0.20)	0.092 (–0.02)
C-10	0.0007 (0.01)	0.0001 (0.003)	0.016 (0.06)	0.009 (0.04)
C-11	0.993 (0.75)	0.986 (0.80)	0.973 (1.22)	0.915 (0.99)
C-12	0.675 (0.11)	0.601 (0.12)	0.732 (0.20)	0.843 (0.18)
C-13	0.972 (0.53)	0.939 (0.55)	0.986 (0.87)	0.957 (0.72)
Se(*E*)	0.952 (14.15)	0.939 (14.99)	0.909 (22.58)	0.905 (18.86)
Series 2 (*Z* isomer)				
Se(*Z*)	0.758 (3.81)	0.686 (3.81)	0.821 (6.70)	0.927 (5.84)
Series 3 ((*Z*)-α-Phenylcinnamonitriles)				
C-8	0.946 (–0.79)	0.930 (–0.83)	0.982 (–1.31)	0.903 (–1.05)
C-9	0.979 (0.34)	0.962 (0.36)	0.932 (0.54)	0.883 (0.44)
C-10	0.892 (0.20)	0.855 (0.20)	0.922 (0.33)	0.875 (0.27)
C-11	0.969 (0.89)	0.939 (0.94)	0.981 (1.47)	0.944 (1.20)

substituents are analyzed individually. Second, the Se atom is quite sensitive to substituent effects, the correlation is normal (positive slope) as was the case with the fluorine in α-fluorocinnamates, and the correlations are comparable to those of C-6 (in both cases there is no significant statistical difference between correlations with σ^{13} and σ^+). Surprisingly, C-7 (the carbonyl carbon), C-11, and C-13 (the ortho and para positions of the phenylseleno group) give better correlations than the β carbon even though none of these atoms is very sensitive to substituent effects ($\rho < 1$). Also, C-10 (the ipso carbon of the phenylseleno group) shows no correlation whatsoever and C-12 (the meta position) provides a modest, but positive, correlation only with σ^-, so there is no alternation of slope in this ring such as is seen in an acyclic side chain. If one compares these observations with those in a series of α-phenylcinnamonitriles[4] (series 3), however, it will be seen that there are similarities whether or not the selenium atom is present. The correlations with σ^{13} values at the ipso, ortho, meta, and para carbons of the (phenylseleno)cinnamates vs the phenylcinnamonitriles are, respectively, as follows: ipso = 0.001 vs –0.946, ortho = 0.993 vs 0.979, meta = 0.675 vs 0.892, and para = 0.972 vs 0.969). The most striking difference here is the lack of any hint of correlation at the ipso carbon of the phenylseleno group, whereas the *reverse* correlation at the ipso carbon of the phenyl group of the α-phenylcinnamonitriles is quite acceptable. One possible explanation for this would be a through-space interaction of the lone pairs of electrons and of the empty d orbitals of the Se atom through the ortho position of the phenylseleno ring, thus skipping any significant interaction with the ipso carbon. Furthermore, the best overall correlations at the other ring positions are observed using σ values: ipso = 0.016 vs 0.982, meta = 0.732 vs 0.922, and para – 0.986 vs 0.981, respectively, for the (phenylseleno)cinnamates vs the phenylcinnamonitriles.

Series 2 (*Z* Isomer). Unfortunately, the unusual low concentrations of the *Z* isomers made it impossible to make ^{13}C assignments sufficient for a meaningful analysis. However, ^{77}Se chemical shifts for 11 of these compounds were obtained (Table II). Whereas the *E* isomers gave a wide chemical shift range (>40 ppm) with good correlations with σ^{13} or σ^+ and slopes ranging from 14.15 to 22.58, the *Z* isomer showed a much narrower range (≈13 ppm), a reasonable correlation *only* with σ^- ($R^2 = 0.927$), slopes ranging from 3.81 to 6.70, and a ^{77}Se chemical shift range some 118–146 ppm further downfield than the corresponding *E* isomers. Interestingly, a plot of the chemical shifts of the *Z* isomers vs those of the *E* isomers gives an R^2 value of 0.804. The same plot with the omission of the *p*-nitro group has a significantly improved R^2 (0.849). From this, it appears that the *p*-nitro group is anomalous in one or the other of these series; however, if the difference in chemical shifts of the *Z* and *E* isomers ($\delta_Z - \delta_E$) is plotted against either σ^{13} or σ^+, a good correlation is obtained ($R^2 = 0.950$), suggesting the opposite conclusion. Both the σ^- correlation and the large, downfield shift of the Se atom in the *Z* series point to an unusual effect in this series, which is perhaps related to the proximity of the relatively large Se atom to the anisotropic, substituted phenyl group. This geometric effect would have no counterpart in the *E* series. Accordingly, the single substituent constant analysis leads to the suggestion that substituent effects in the *Z* series may be greatly influenced by a field effect. The relatively small effect of substituents in this series may accord with this suggestion.

The fact that σ^- correlations are obtained for the *Z* series is puzzling, but not without precedent in NMR work. Pomerantz et al. found σ^- correlations for the chemical shifts of both ^{31}P and ^{15}N, as well as for several ^{13}C atoms and for some different coupling constants, in *N*-aryl-*P,P,P*-triphenyl-λ^5-azenes,[12] and Krabbenhoft found that a combination of σ^- and σ^+ gave the best correlations for the shifts of the β-carbon atoms in α,β,β-trichlorostyrenes.[13] The substantial downfield shift could result either from diminished electron density at the target site or from the presence of a stronger local magnetic field due to the anisotropy of the benzene ring. Thus, substituent effects at the selenium atom may reflect not only changes in electron density resulting from inductive and resonance effects, but also, perhaps as importantly, field effects related to the substituent's influence on the anisotropy of the ring. Consequently, if the effect on anisotropy is of significance, a dual-parameter analysis should be helpful because it should reveal for the *Z* series a stronger dependence on σ_I, which also incorporates field effects, than should be found for the *E* series.

DSP Analysis. Series 1 (*E* Isomer). The results of DSP analyses of ^{77}Se chemical shifts using Taft's σ_I and σ^0_R parameters[4] are collected in Table V. Meta and para substituents were treated separately because they typically show different mixes of resonance and polar/field demands. The R^2 values for the selenium atom in this series are excellent, the *F* value for the para isomer being the best of the lot, although all are acceptable. It should be noted that the resonance contribution from the meta isomers appears to be quite low in comparison with other λ (ρ^0_R/ρ_I) values. Nevertheless, it appears obvious that the selenium atom, like fluorine, produces normal substituent effects in this series. The DSP treatment also gives excellent results at the ortho and para (C11 and C13) positions of the phenylseleno group and a much improved correlation at the meta (C12) position, although it should be observed that there is a considerably reduced resonance contribution at the meta position in the (phenylseleno)cinnamates vs the phenylcinnamonitriles.

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Table V. ^{77}Se and ^{13}C DSP Analyses for Ethyl α-(Phenylseleno)cinnamates and α-Phenylcinnamonitriles[a,b]

atom	series	isomer	ρ_I	ρ°_R	b	R^2	F (λ)
Se	1(*E*)	para	13.3132	44.0062	352.61	0.9878	325.1 (3.31)
Se	1(*E*)	meta	10.9532	0.1481	351.83	0.9756	79.9 (0.01)
Se	2(*Z*)	para	6.5067	9.9588	477.27	0.8192	13.6 (1.53)
C6	1(*E*)	para	11.2500	31.8716	131.74	0.9500	76.0 (2.83)
C6	1(*E*)	meta	9.8150	1.7363	130.93	0.8420	10.7 (0.18)
C11	1(*E*)	para	0.7983	2.0692	131.68	0.9721	139.1 (2.59)
C11	1(*E*)	meta	0.8674	0.4670	131.67	0.9916	237.3 (0.54)
C12	1(*E*)	para	0.2800	0.2805	129.05	0.9295	52.8 (1.00)
C12	1(*E*)	meta	0.2077	0.0674	129.00	0.8695	13.3 (0.32)
C13	1(*E*)	para	0.7921	1.2931	127.04	0.9799	154.8 (1.63)
C13	1(*E*)	meta	0.7710	0.4397	127.02	0.9817	107.2 (0.57)
C8	3(*Z*)	para	−1.2508	−1.7401	134.43	0.9771	170.9 (1.39)
C8	3(*Z*)	meta	−1.4087	−0.7032	134.44	0.9765	83.1 (0.50)
C9	3(*Z*)	para	0.3202	0.9672	125.96	0.9354	58.0 (3.02)
C9	3(*Z*)	meta	0.3091	0.2519	125.95	0.9480	36.4 (0.81)
C10	3(*Z*)	para	0.2803	0.4628	129.06	0.9300	53.1 (1.65)
C10	3(*Z*)	meta	0.3386	0.2864	129.03	0.9619	50.5 (0.85)
C11	3(*Z*)	para	1.2334	2.1252	129.15	0.9652	110.8 (1.72)
C11	3(*Z*)	meta	1.3104	0.7327	129.11	0.9693	63.2 (0.56)

[a] Based on the equation $\delta_X = \rho_I\sigma_I + \rho^\circ_R\sigma^\circ_R + b$. [b] Dual substituent parameters of −0.11 and −0.03 for σ_I and σ°_R, respectively, for the *p*-phenyl group have been calculated by a statistical analysis of available NMR data found in ref 4. Other values of σ_I and σ°_R are also found in ref 4.

Series 2 (*Z* Isomer). Although the DSP treatment of the ^{77}Se chemical shifts of the para isomer are better than those provided by single substituent analysis using either σ^{13} or σ^+, they still fall short of that provided by the σ^- value. The DSP analysis does confirm, however, that, as suggested earlier, there is a considerably greater contribution from field effects in this case (λ is 1.53 for the para-substituted *Z* isomers as compared to 3.31 for the analogous *E* isomers).

Series 3 (α-Phenylcinnamonitriles). Interestingly, the DSP analysis of the phenyl substituent shows a marked improvement in correlations at the ipso and meta positions (C8 and C10); however, there is no improvement at the para position and a somewhat poorer correlation at the ortho position. The λ values for the ortho, meta, and para positions are almost invariably higher than the equivalent positions in the (*E*)-(phenylseleno) compounds, which might be predicted since the resonance contribution is not filtered through the selenium atom in this series.