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Selenophene Series. III (1). Substituent Effect on the Rate of Reaction of Various
2-Bromo-3-nitro-5-X-selenophenes with Piperidine in Ethanol

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We have recently shown that the reactivity of the bromo-nitroselenophenes Ia and IIa towards the nucleophilic reagents, piperidine and sodium thiophenoxide, is greater than that of the corresponding thiophenes (Ib and IIb) (1).

We have also observed (3) that the rate of nucleophilic substitution in the thiophene series IIIb may be correlated by the Hammett equation (4) using the *para* substituent constants.

In this paper we report on the application of same Hammett equation to the piperidino-debromination in 2-bromo-3-nitro-5-X-selenophenes (IIIa).

The main objective of this research was a comparison, based on the results of a parallel investigation in the thiophene series (3), of the transmission of electronic effects operating through the selenophene and the thiophene rings. It must be pointed out that, in the selenophene series, the validity of the Hammett equation has never been hitherto verified, except in the case of the polarographic reduction of some nitroselenophenes (5).

In Table I the rate constants are reported together with the thermodynamic parameters. In Fig. I the logarithms of the rate constants at 20° for the reaction of the selenophene derivatives and, for a comparison, those previously measured in the thiophene series are plotted against the σ^- values reported in the literature (6). All the experimental points, except the one corresponding to the reaction between 2-bromo-3-nitro-5-methylsulphonylselenophene, fall on a straight line and a ρ value equal to + 3.15 may be calculated (correlation coefficient, $r = 0.995$). In the case of the sulphonyl derivative a better agreement is found using the σ^- value (0.840) determined by F. G. Bordwell and H. M. Andersen (7). An analogous deviation has been observed by ourselves in the thiophene series (3).

The measured ρ value corroborates our previous finding

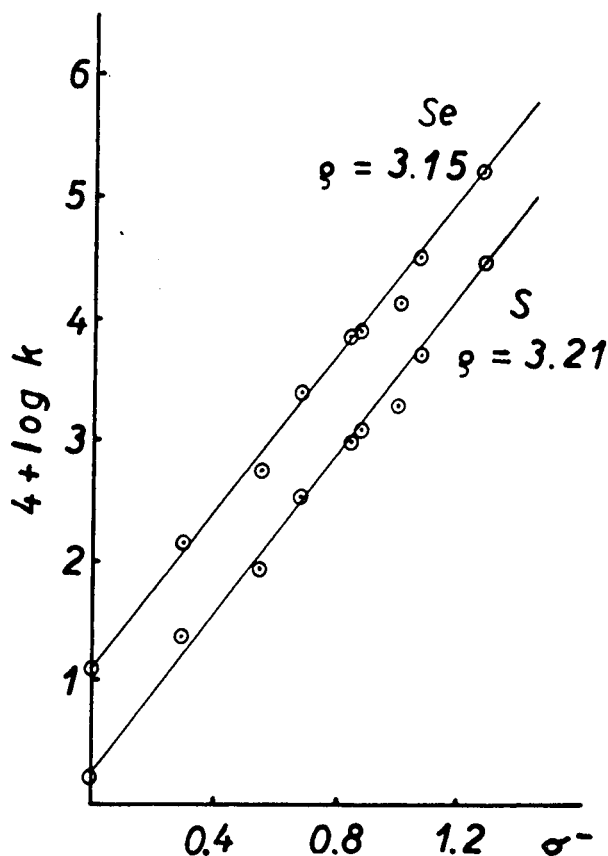
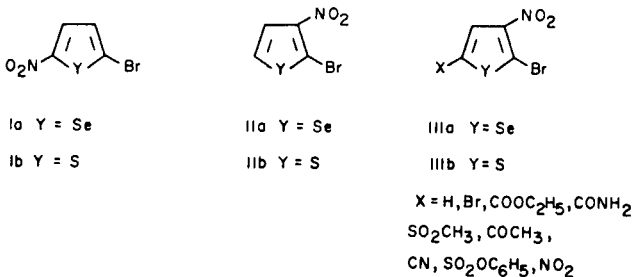


Figure 1

that in the five-membered heterocycles the position 5 is, with respect to the position 2, a *para*-like position from which the substituent may operate with electronic effects only. The required use of σ^- values and the high ρ value suggest that the conjugative effects predominate over the inductive ones and that the reaction center is sensitive to the electronic effects of the substituent.

The comparison with the results obtained in the thiophene series (3) (see Fig. I) appears to be particularly interesting.

The higher reactivity of the selenophene derivatives compared to the thiophene derivatives, which we have observed in some other cases of nucleophilic substitution, appears confirmed. Moreover the measured value ($\rho = + 3.15$) is

TABLE I

Kinetic Data for the Reaction Between
2-Bromo-3-nitro-5-X-selenophenes and Piperidine in Ethanol

X	$10^2 k, \text{l mol}^{-1} \text{sec}^{-1}$, at various temperatures (1)					E_{exp} (2) kcal/mole	ΔH^\ddagger (2) kcal/mole	$-\Delta S^\ddagger$ (3) u.e.	σ^- (4)
	0.00°	9.92°	19.92°	29.77°	40.05°				
H			0.113	0.247	0.534	14.1	13.5	25.8	0.000
Br			1.42	2.83	5.64	12.5	11.9	26.2	0.289
CONH ₂			5.58	11.67	22.35	12.6	12.0	23.3	0.552
COOC ₂ H ₅			24.43	45.70	85.90	11.4	10.8	24.3	0.678
SO ₂ CH ₃		36.50	71.20	130		10.9	10.3	24.1	1.049
COCH ₃		39.69	72.90	128		10.0	9.4	27.0	0.874
CN	25.85	47.50	99.90			10.8	10.2	23.8	0.997
SO ₂ OC ₆ H ₅	110	187.4	329			8.7	8.1	28.3	1.065 (5)
NO ₂	542	1007	1650			8.9	8.3	24.5	1.270

(1) The rate constants are accurate to better than $\pm 2\%$. (2) The probable error is 0.3 Kcal/mole. (3) At 20°. (4) H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953); L. N. Fergusson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, N. Y., p. 415 (1959). (5) C. Dell'Erba and D. Spinelli, *Tetrahedron*, 21, 1061 (1965).

TABLE II

2-Bromo-3-nitro-5-X-selenophenes

X	Crystallization Solvent	Color and Crystal Form	M.P.	Found (%)		Formula	Required (%)	
				N	Br		N	Br
H (1)	ligroin	colorless needles	85°					
Br (2)	light petroleum	colorless needles	87°					
CONH ₂	ethanol	yellow needles	232°	9.42	26.34	C ₅ H ₃ BrN ₂ O ₃ Se	9.40	26.85
COOC ₂ H ₅	ethanol	colorless needles	96°	4.60	25.02	C ₇ H ₆ BrNO ₄ Se	4.28	24.46
SO ₂ CH ₃ (3)	ethanol	colorless needles	145°	4.21	24.36	C ₅ H ₄ BrNO ₄ SSe	4.20	24.02
COCH ₃	ethanol	colorless needles	145°	4.73	26.41	C ₆ H ₄ BrNO ₃ Se	4.71	26.94
CN (4)	ethanol	yellow plates	174°	10.21	28.02	C ₅ HBrN ₂ O ₂ Se	10.00	28.57
SO ₂ OC ₆ H ₅	ligroin	colorless needles	81°	3.51	20.01	C ₁₀ H ₆ BrNO ₅ SSe	3.41	19.46
NO ₂ (2)	ligroin	yellow prisms	128°					

(1) L. Chierici, C. Dell'Erba and D. Spinelli, *Ann. Chim.*, 55, 1069 (1965). (2) S. Umezawa, *Bull. Chem. Soc. Japan*, 11, 775 (1936); see *Chem. Abstr.*, 31, 2211 (1937). (3) This product was prepared from 2-bromo-5-methylsulphonyl-selenophene by nitration. The last product (m.p. 54°, colorless plates from ligroin. Calcd. for C₅H₅BrO₂SSe: Br, 27.78. Found: 27.00) was prepared from 2-bromo-5-selenophensulphonyl chloride according to J. Cymerman and J. L. Lowe [*J. Chem. Soc.*, 6166 (1949)]. (4) This product was prepared from 2-bromo-5-cyanoselenophene by nitration. The last product (m.p. 55°, colorless crystals from methanol/water. Calcd. for C₅H₂BrNSe: N, 5.96. Found: 6.06) was prepared from 2-bromo-5-selenophenaldoxime according to P. Reynaud and R. Delaby [*Bull. Soc. Chim. France*, 1614 (1955)].

TABLE III

2-N-Piperidyl-3-nitro-5-X-selenophenes

X	Crystallization Solvent	Color and Crystal Form	M.P.	Found N%	Formula	Required N%	λ max (μ)	log ϵ
H (1)	light petroleum	orange prisms	82°				408	3.77
Br (2)	light petroleum	yellow needles	80°	8.38	C ₉ H ₁₁ BrN ₂ O ₂ Se	8.28	414	3.80
CONH ₂	ethanol	yellow needles	231°	14.01	C ₁₀ H ₁₃ N ₃ O ₃ Se	13.91	400	3.79
COOC ₂ H ₅ (3)	ligroin	yellow needles	74°	8.60	C ₁₂ H ₁₆ N ₂ O ₄ Se	8.46	394	3.78
SO ₂ CH ₃	ethanol	yellow plates	143°	8.39	C ₁₀ H ₁₄ N ₂ O ₄ SSe	8.31	386	3.79
COCH ₃	ligroin	yellow needles	115°	9.39	C ₁₁ H ₁₄ N ₂ O ₃ Se	9.30	358	4.20
CN	ethanol	yellow needles	134°	14.83	C ₁₀ H ₁₁ N ₃ O ₂ Se	14.79	390	3.78
SO ₂ OC ₆ H ₅	ethanol	yellow plates	118°	6.87	C ₁₅ H ₁₆ N ₂ O ₅ SSe	6.75	384	3.78
NO ₂	methanol	yellow plates	130°				414	4.15

(1) L. Chierici, C. Dell'Erba and D. Spinelli, *Ann. Chim.*, **55**, 1069 (1965). (2) Br%: Found: 23.54. Required: 23.67. (3) Se%: Found: 23.50. Required: 23.87.

close to the one measured in the thiophene series ($\rho = + 3.21$) and this result may be considered as indicative of the similarity in the transmission of the electronic effects through the π sextet (8).

EXPERIMENTAL

Synthesis and Purification of Materials.

The 2-bromo-3-nitro-5-X-selenophenes and the 2-N-piperidyl-3-nitro-5-X-selenophenes were prepared as described for the thiophene derivatives (3).

The relevant physical and analytical data are reported in Tables II and III.

Kinetic Measurements.

The reaction kinetics were followed as previously described (9). The wavelength and the logarithm of the molar extinction coefficients of the 2-N-piperidyl-3-nitro-5-X-selenophenes are reported in Table III. The concentrations were 1×10^{-4} M for the 2-bromo-5-X-selenophenes and 6×10^{-4} M for piperidine. The ethanol used was purified by standard methods.

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(8) In the selenium and sulfur compounds in which the heteroatom is in a linear chain [see for instance the hydrolysis of C₆H₅-CH₂-CO-Y-C₆H₄-R, where Y = S, Se, in J. Gosselck, *Angew. Chem. Internat. Ed. Engl.*, **2**, 660 (1963) and references therein], when substituents are present in the phenyl ring bound to the heteroatom, Hammett correlations with very close ρ values are observed. However in this case the situation is different since in the transmission of the electronic effects only the two heteroatoms participate.

(9) D. Spinelli, A. Salvemini and C. Dell'Erba, *Ann. Chim.*, **54**, 869 (1964).

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