

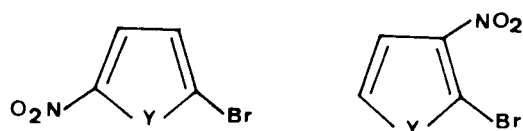
Selenophene Series. V (1).  
Reactivity of 3-Bromo-2-nitroselenophene Towards Nucleophilic Reagents.  
Comparison with other Selenophene and Thiophene Bromonitroderivatives.

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In various papers we have reported kinetic studies of nucleophilic substitution reactions on 2-halogenitroselenophenes (2). Particularly we observed that the reactivity of bromonitroselenophenes Ia and IIa (reaction center in the  $\alpha$ -position) towards the nucleophilic reagents is greater than that of the corresponding bromonitrothiophenes (Ib and IIb) (3).

In this paper we report the results of a kinetic study on thiophenoxy and selenophenoxy debromination reactions of IIIa and on the selenophenoxy debromination reaction of IIa.

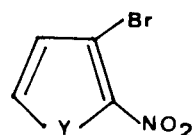


Ia Y = Se

Ib Y = S

IIa Y = Se

IIb Y = S



IIIa Y = Se

IIIb Y = S

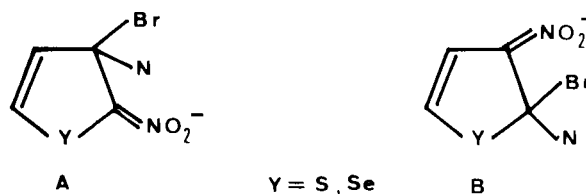
The main objective of this research was to determine, by comparison with the results previously obtained from the parallel investigations on the thiophene derivatives IIb and IIIb (4) and on 2-bromo-3-nitroselenophene IIa, the effect of the heterocyclic heteroatom on the reactivity towards nucleophilic reagents (sodium thiophenoxide and selenophenoxide) of bromonitroderivatives IIIa and IIIb (reaction center in the  $\beta$ -position) and therefore on the relative reactivity of the "ortho-like" isomers IIa and IIIa, IIb and IIIb.

In Table II rate constants, thermodynamic parameters and reactivity ratios are reported together with the results previously obtained for IIa, IIb and IIIb.

The results show that both in thiophenoxy and in selenophenoxy debromination reactions the selenophene derivative IIIa is more reactive than the thiophene derivative IIIb ( $k_{IIIa}/k_{IIIb} \approx 4$ ) and that this reactivity ratio is similar to that obtained for IIa and IIb ( $k_{IIa}/k_{IIb} \approx 4$ ).

Therefore these results point out that also when the reaction center is in the  $\beta$ -position (as in the reaction of IIIa and IIIb derivatives with nucleophilic reagents) the nature of the heteroatom affects the reactivity of these heterocyclic systems (the selenophenic compound has a greater susceptibility to nucleophilic attack compared to that of the thiophene compound), but the  $k_{IIIa}/k_{IIa}$  and  $k_{IIIb}/k_{IIb}$  ratios (see Table II) are scarcely affected by the change from S to Se both in the heterocyclic heteroatom and in the nucleophilic anion.

This research also confirms our previous hypothesis (3) that the structures A and B are the most important resonance forms when describing the electronic distribution of the reaction intermediate in the nucleophilic substitutions on bromonitro derivatives II and III: however by changing both the heterocyclic heteroatom and its position with respect to the reaction center the stability of these intermediates appears to be not differently affected.



Y = S, Se

N =  $C_6H_5S$ ,  $C_6H_5Se$

#### EXPERIMENTAL

The preparation of 2-bromo-3-nitroselenophene is described in reference 5.

3-Bromo-2-nitroselenophene.

To a solution of 3-bromoselenophene (10 g.) in acetic anhydride (15 ml.) a mixture of concentrated nitric acid ( $d = 1.4$ , 7.7 ml.) and acetic anhydride (19 ml.) was added with stirring at  $-10^\circ$ . The mixture was stirred at the same temperature for an additional 20

TABLE I

Physical, Analytical and Spectroscopic (U.V.) Data of Thiophenoxy and Selenophenoxy Debromination Products Obtained from 2-Bromo-3-nitro- (IIa) and 3-Bromo-2-nitroselenophene (IIIa)

	M.P. °C	$\lambda$ max m $\mu$	log $\epsilon$
Phenyl 2-(3-nitro)-selenienylselenide (1)	100-101°	382	3.82
Phenyl 3-(2-nitro)-selenienylselenide (2)	111-112°	400	4.00
Phenyl 3-(2-nitro)-selenienylsulfide (3)	102-103°	386	4.01

(a) in methanol. (1) Found: C, 36.40; H, 2.15; N, 4.33; Se, 47.80.  $C_{10}H_7NO_2Se_2$  requires: C, 36.27; H, 2.11; N, 4.23; Se, 47.70. (2) Found: C, 36.23; H, 2.13; N, 4.31; Se, 47.93;  $C_{10}H_7NO_2Se_2$  requires: C, 36.27; H, 2.11; N, 4.23; Se, 47.70. (3) Found: C, 42.50; H, 2.48; N, 5.03; Se, 27.80;  $C_{10}H_7NO_2SSe$  requires: C, 42.22; H, 2.46; N, 4.93; Se, 27.78.

TABLE II

Kinetic and Thermodynamic Data of Reaction with Sodium Thiophenoxide and Selenophenoxide of Bromonitroselenophenes and Bromonitrothiophenes

Substrate Nucleophilic Reagent	Bromonitroselenophenes				Bromonitrothiophenes			
		$C_6H_5SNa$		$C_6H_5SeNa$		$C_6H_5SNa$ (d)		$C_6H_5SeNa$ (d)
T (°C)	0	10.10	20.02	0	10.10	20.02	20.02	20.02
$k_{III}$ (+) (a)	0.15	0.37	0.85	1.16	2.57	5.56	0.23	1.52
$\Delta H^\ddagger$ (b)			13.3			11.9	13.6	12.6
$-\Delta S^\ddagger$ (c)			13.4			14.5	14.9	14.3
$k_{II}$ (+) (a)			0.47 (e)	0.44	1.00	2.17	0.12	0.53
$\Delta H^\ddagger$ (b)			12.7 (e)			12.2	13.8	11.8
$-\Delta S^\ddagger$ (c)			16.6 (e)			15.3	15.8	19.3
$k_{III}/k_{II}$			1.80			2.56	1.92	2.84

(+)  $k_{III}$  and  $k_{II}$  are expressed in  $l\ mol^{-1}\ sec^{-1}$  and point out respectively the rate constants of the reactions on the 3-bromo-2-nitro-derivatives (IIIa and IIIb) and on the 2-bromo-3-nitroderivatives (IIa and IIb). (a) The probable error is  $\pm 4\%$ . (b) In  $Kcal\ mol^{-1}$  at  $20^\circ$ . The probable error is  $\pm 0.3\ Kcal\ mol^{-1}$ . (c) In e.u. at  $20^\circ$ . (d) See reference (4). (e) See reference (2).

minutes, poured onto ice and extracted with ether. The ethereal extracts were washed with sodium bicarbonate solution, followed by water and dried over sodium sulfate. Removal of the ether gave a brown oil which was chromatographed on silica-gel: elution with 1:2 (v/v) benzene-petroleum ether (b.p. 80-100°) gave two solid products. The first (1.1 g.), crystallized from petroleum ether (b.p. 80-100°) consisted of yellow orange needles, m.p. 87°.

*Anal.* Calcd. for  $C_4H_2BrNO_2Se$ : C, 18.82; H, 0.78; Br, 31.34; N, 5.50. Found: C, 18.74; H, 0.79; Br, 30.90; N, 5.54.

The second product (1.25 g.) crystallized from petroleum ether (b.p. 80-100°) as yellow needles, m.p. 90°.

*Anal.* Calcd. for  $C_4H_2BrNO_2Se$ : C, 18.82; H, 0.78; Br, 31.34; N, 5.50. Found: C, 18.90; H, 0.78; Br, 31.28; N, 5.57.

The two products were identified as 2-nitro-4-bromoseleno-

phene and 3-bromo-2-nitroselenophene respectively, on the basis of their reactivity.

Both, upon dehalogenation with copper in boiling acetic acid, gave 2-nitroselenophene, identified by comparison with an authentic sample (6). Moreover with sodium thiophenoxide and selenophenoxide the isomer with m.p. 90° gave respectively phenyl 3-(2-nitro)selenienyl sulfide and phenyl 3-(2-nitro)selenienyl selenide, isospectral with the analogous thiophene derivatives.

The sulfides and selenides were prepared as described in previous papers (2,3,4) and their physical, analytical and spectroscopic (U.V.) data are given in Table I.

Reaction rates were measured by the spectrophotometric method reported in previous papers (2,3,4).

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## REFERENCES

- (1) Part IV: D. Spinelli, G. Guanti and C. Dell'Erba, *Ric. Sci.*, **38**, 1048 (1968).
- (2) L. Chierici, C. Dell'Erba, A. Guareschi and D. Spinelli, *Ann. Chim.*, (Rome), **57**, 632 (1967); C. Dell'Erba, A. Guareschi and D. Spinelli, *J. Heterocyclic Chem.*, **4**, 438 (1967).
- (3) D. Spinelli, C. Dell'Erba and G. Guanti, *Ann. Chim.* (Rome), **55**, 1252, 1260 (1965).
- (4) D. Spinelli, G. Guanti and C. Dell'Erba, *Ric. Sci.*, **38**, 1051 (1968); G. Guanti, C. Dell'Erba and D. Spinelli, *Gazz. Chim. Ital.*, **100**, 184 (1970).
- (5) L. Chierici, C. Dell'Erba and D. Spinelli, *Ann. Chim.*, (Rome), **55**, 1069 (1965).
- (6) S. Umezawa, *Bull. Chem. Soc. Japan*, **11**, 775 (1936); *Chem. Abstr.*, **31**, 2211 (1937).

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