Selenation of 1,5-Naphthoquinones: Novel Synthesis of Naphthopyridoselenazines

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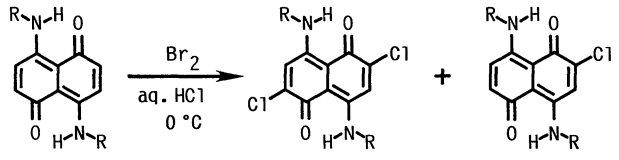
Selenation of 2-chloro- and 2,6-dichloro-1,5-naphthoquinones with benzeneselenolate ion, generated from diphenyl diselenide and tributylphosphine in an alkaline medium, afforded 2-phenylseleno- and 2,6-bis(phenylseleno)-1,5-naphthoquinones in excellent yields. Reaction of halo-1,4-naphthoquinones with 3-amino-2-pyridineselenolate ion generated from bis(3-amino-2-pyridyl) diselenide gave naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]-selenazines and pyrido[2,3-*b*]pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*][1,4]selenazines in high yields.

Phenothiazinones[1] and phenoselenazinones[2] are known as potent dyes for semiconductor lasers used for optical information recording media. We previously synthesized 4*H*-benzo[*a*]phenothiazin-4-ones[3] and 4*H*-benzo[*a*]phenoselenazin-4-ones[4] and found that they show absorptions in the near infrared. In a previous report[5] we described a new efficient selenation method for conversion of 2-halo-1,4-naphthoquinones into 2-phenylseleno-1,4-naphthoquinones. We herein describe the application of this new selenation to the synthesis of naphthopyridoselenazines using bis(3-amino-2-pyridyl) diselenide as a selenating reagent. We also report the selenation of 2-chloro- and 2,6-dichloro-4,8-bis(alkylamino)-1,5-naphthoquinones.

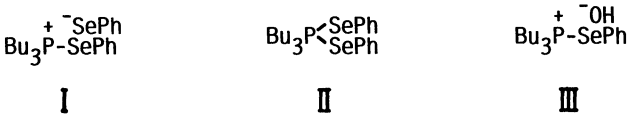
Results and Discussion

Preparation of Seleno-Substituted 1,5-Naphthoquinones. We were interested in the reaction site of benzeneselenolate ion to 2-chloro-1,5-naphthoquinones and examined the selenation of 2,6-dichloro- and 2-chloro-4,8-bis(2-propylamino)-1,5-naphthoquinones (**3** and **5**), and 2-chloro-4,8-bis(methylamino)-1,5-naphthoquinone (**6**). We found that 2,6-dichloro- and 2-chloronaphthoquinones **3** and **5** were obtainable by the reaction of 4,8-bis(2-propylamino)-1,5-naphthoquinone[6] (**1**) with bromine in hydrochloric acid in 45 and 26% yield, respectively. Chlorination of 4,8-bis(methylamino)-1,5-naphthoquinone[6] (**2**) in the same manner afforded chloronaphthoquinone **6** in 36% yield, together with 2,6-dichloronaphthoquinone **4** (yield 22%) (Scheme 1).



Scheme 1.

With chloronaphthoquinones **3**, **5**, and **6** in hand, we then attempted the selenation. A solution of benzeneselenolate ion was prepared as follows. To a vigorously stirred tetrahydrofuran (THF) solution of 1.10 molar equiv of diphenyl diselenide and 1.20 molar equiv of tributylphosphine, was added 2.20 molar equiv of an aqueous NaOH solution. The mixture was vigorously stirred for 15 min during which time the yellow two-phase solution became colorless and homogeneous, a mixture containing benzeneselenolate ion being formed. The mechanism for the generation of selenolate ion can be postulated as we described earlier:[5] A selenophosphonium ion **I** and/or a pentavalent phosphorus species **II** are initially formed in the reaction of diphenyl diselenide and a phosphine, and addition of NaOH liberates benzenselenolate ion and the phosphonium ion **III**, from which is



further generated selenolate ion together with phosphine oxide by the action of NaOH. In line with this mechanism, tributylphosphine oxide was be isolated quantitatively. Treatment of dichloronaphthoquinone **3** with a solution of benzeneselenolate ion thus obtained at room temperature yields bisphenylselenated naphthoquinone in 88% yield. The regioselectivity of the phenylseleno group, however, could not be determined directly on the basis of the spectral data. The structure was eventually assigned as 4,8-bis(2-propylamino)-2,6-bis(phenylseleno)-1,5-naphthoquinone (**7**) by X-ray analysis (see Fig. 1 and Tables 2 and 3). Consequently, the selenation presumably starts with the attack of benzeneselenolate ions on both carbons α to the carbonyl groups, i.e., on each carbon attached to the chloro group, of 2,6-dichloro-1,5-naphthoquinone **3**, followed by β-elimination of chloride ions to form 2,6-bis(phenylseleno)-1,5-naphthoquinone **7**.

The selenation of **5** and **6** using diphenyl diselenide

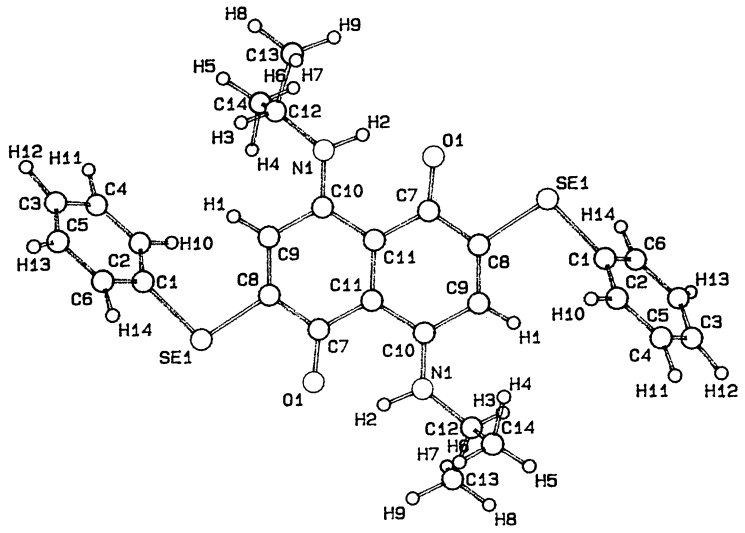
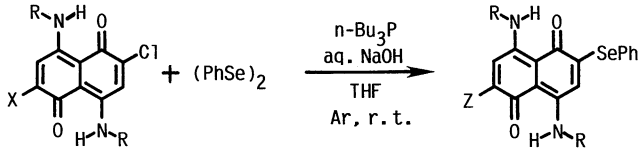
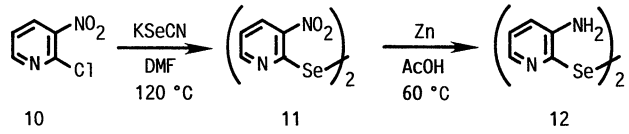


Fig. 1. An ORTEP view of **7** together with the atom numbering system.



Scheme 2.



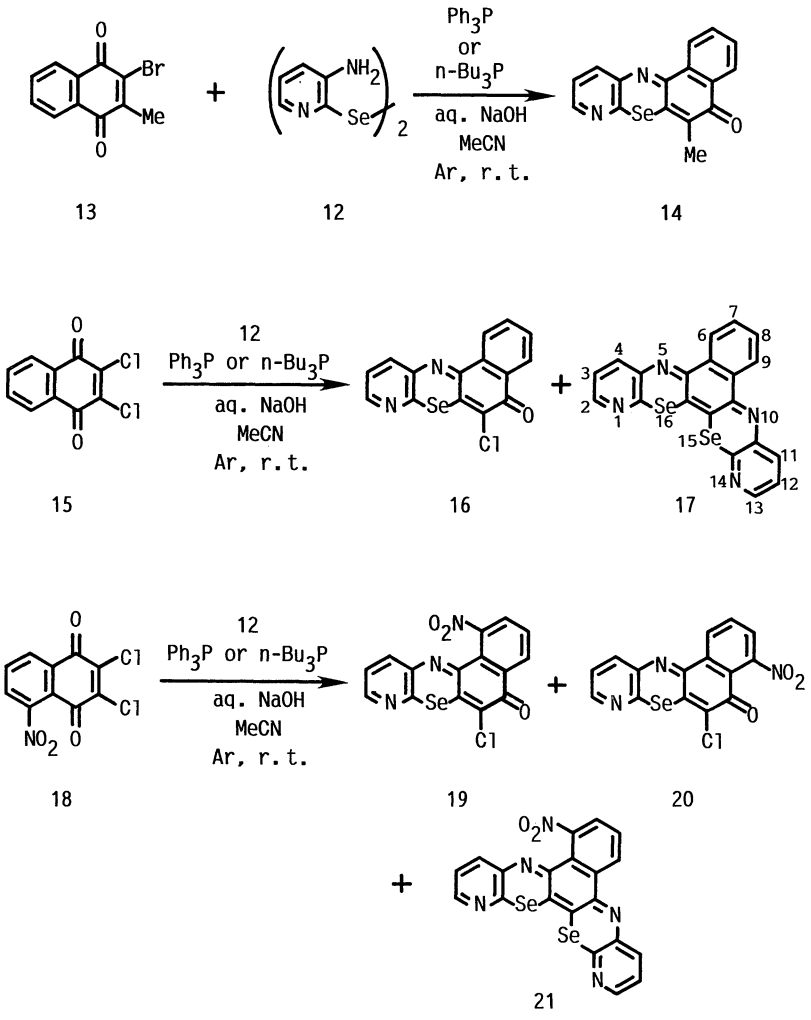
Scheme 3.

(0.55 molar equiv), tributylphosphine (0.60 molar equiv), and an aqueous NaOH (1.10 molar equiv) solution afforded phenylselenated 4,8-bis(2-propylamino)- and 4,8-bis(methylamino)-1,5-naphthoquinones **8** and **9** in 94 and 89% yield, respectively. In the ^{1}H NMR spectrum, the protons on C-3 and C-7 of **7** appeared at δ=6.39. The protons on C-3 of **8** and **9** appeared at δ=6.46 and 6.51, respectively. From the mechanistic point of view, as shown above in the selenation of **3** as well as the ^{1}H NMR data, **8** and **9** were tentatively assigned as 4,8-bis(2-propylamino)- and 4,8-bis(methylamino)-2-phenylseleno-1,5-naphthoquinones, respectively (Scheme 2).

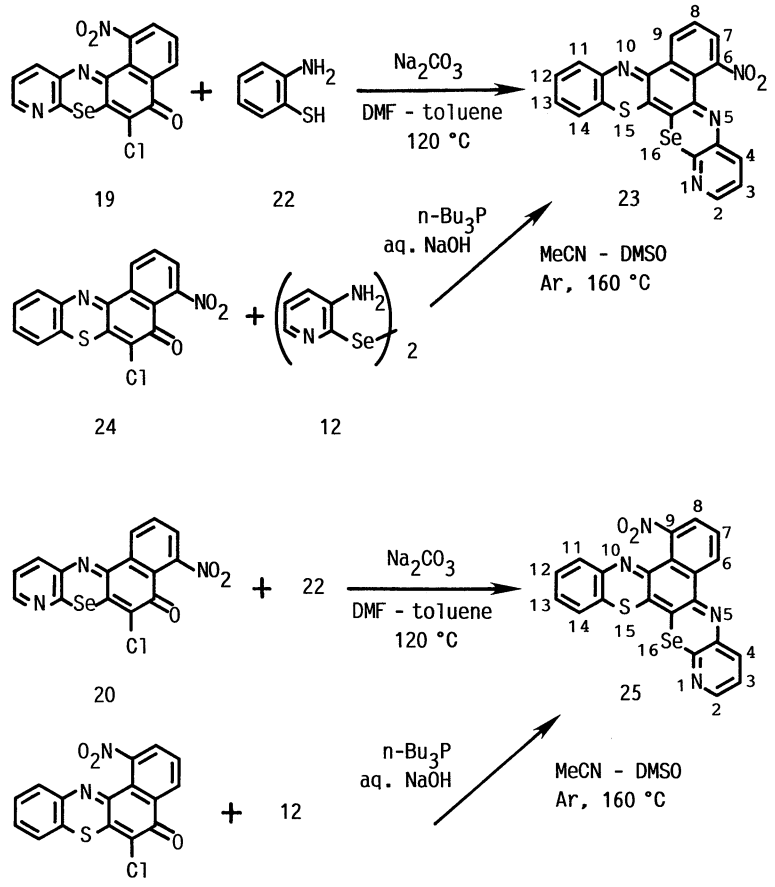
Preparation of Naphthopyridoselenazines. Recently we found that the reaction of naphthoquinones with zinc 2-aminobenzeneselenenate, prepared from bis(2-nitrophenyl) diselenide and zinc in acetic acid, gave phenoselenazinones in high yield.[4] In order to prepare naphthopyridoselenazine derivatives in a similar manner as above, we first attempted to prepare zinc 3-amino-2-pyridineselenenate by the reaction of bis(3-nitro-2-pyridyl) diselenide (**11**) with zinc. The reaction, however, did not give zinc 3-amino-2-pyridineselenenate but instead gave bis(3-amino-2-pyridyl) diselenide (**12**) in good yield. Thus, dipyridyl diselenide **12** was obtained in 53% yield by the reaction of 2-chloro-3-nitropyridine (**10**) with potassium selenocyanate in DMF at 120 °C followed by reduction with zinc and acetic acid (Scheme 3). Fortunately, the 3-amino-2-pyridineselenolate ion was found to be generated from the dipyridyl diselenide **12** on treatment with triphenyl- or tributylphosphine in an alkaline medium. An acetonitrile solution of dipyridyl diselenide **12** (0.58 molar equiv) and triphenylphosphine (1.25 molar equiv) was vigirously stirred under argon at room temperature. To this was added an aqueous NaOH (1.08 molar equiv) solution, and the mixture was vigorously stirred for 15 min to give a mixture containing 3-amino-2-pyridineselenolate ion. Treatment of 2-bromo-3-methyl-1,4-naphthoquinone (**13**) with a solution of 3-amino-2-pyridineselenolate ion at room temperature gave 6-methyl-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]selenazin-5-one (**14**) in 91% yield, which would have been formed via selenation and subsequent condensation between the quinone carbonyl and aromatic amino group (or vice versa). 3-Amino-2-pyridineselenolate ion formed from diselenide **12** (0.58 molar equiv) and tributylphosphine (1.25 molar equiv) in place of triphenylphosphine in an alkaline medium (1.08 molar equiv) was also effective, giving **14** in 93% yield. The reaction of 2,3-dichloro-1,4-naphthoquinone (**15**) with 3-amino-2-pyridineselenolate ion generated from diselenide **12** (0.69 molar equiv) and triphenylphosphine (1.46 molar equiv) afforded 6-chloro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]selenazin-5-one (**16**) and pyrido[2,3-

b]pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*][1,4]selenazine (**17**) in 61 and 18% yield, respectively. When tributylphosphine was used instead of triphenylphosphine, **16** and **17** was formed in 20 and 54% yield, respectively. The bisselenated product **17** was formed predominantly when tributylphosphine was used. This is presumably because of higher reducing ability of Bu_3P compared to Ph_3P, which caused a rapid formation and thus higher concentration of selenolate ion in the reaction mixture (reaction time: 20 min for Bu_3P vs. 1 h for Ph_3P), resulting in the formation of a larger amount of the bisselenated product **17**. A similar result was obtained in the following reaction. Treatment of 2,3-dichloro-5-nitro-1,4-naphthoquinone[7] (**18**) with 3-amino-2-pyridineselenolate ion gave two regioisomeric nitro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]-selenazin-5-ones (**19** and **20**), and a bisselenated product, 6-nitropyrido[2,3-*b*]pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*][1,4]selenazine (**21**), in 47, 19, and 17% yield, respectively, when triphenylphosphine was used, and in 30, 18, and 40% yield, respectively, when tributylphosphine used (Scheme 4).

Though two regioisomeric products **19** and **20** could not be distinguished from each other by examining their spectral data, they were unambiguously assigned to be a 6-chloro-1-nitro compound **19** and a 6-chloro-4-nitro compound **20**, respectively, by the correlation with known compounds 6-chloro-4-nitro-5*H*-benzo[*a*]phenothiazin-5-one[8] (**24**) and the corresponding 6-chloro-1-nitro isomer[8] **26**. Two reference compounds **24** and **26** were respectively subjected to selenation with dipyridyl diselenide **12** and tributylphosphine in a mixture of acetonitrile, dimethyl sulfoxide and an aqueous NaOH solution (160 °C), giving 6-nitrobenzo[*b*]pyrido-[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*]-[1,4]thiazine (**23**) and the 9-nitro isomer **25** in 32% and 52% yield. The reaction of the above-mentioned product **19** with 2-aminobenzenethiol (**22**) and Na_2CO_3 in DMF–toluene at 120 °C gave naphthothiazine, which was readily identified as the 6-nitro compound **23** in terms of the spectral data. On the other hand, the naphthothiazine obtained from the reaction of **20** with **22** was shown to be identical to the 9-nitro isomer **25** (Scheme 5). Thus, two isomeric products **19** and **20**



Scheme 4.



Scheme 5.

were identified to have 6-chloro-1-nitro and 6-chloro-4-nitro structures, respectively.

Since gallium arsenide, a semiconductor for optical recording media, emits a laser light at 800—830 nm, optical absorption in the near infrared region is required for dyes used in optical recording. In previous reports we described that 4*H*-benzo[*a*]phenothiazin-4-ones[3] and 4*H*-benzo[*a*]phenoselenazin-4-ones[4] absorbed at 750—770 nm. The naphthopyridoselenazines and phenylselenated 1,5-naphthoquinones prepared in the present work unfortunately do not show satisfactory absorptions compatible with semiconductor lasers: The naphthopyridoselenazines and naphthopyridoselenazine derivatives absorb at wavelengths in a region of 470—573 nm, whereas phenylseleno- and bis(phenylseleno)-1,5-naphthoquinones absorb at 664—666 nm. The λ_{max} values of these compounds are given in Table 1.

Experimental

General. Mps were recorded on a Yanaco micro-melting point apparatus and are uncorrected. IR spectra were measured on KBr discs on a JASCO A-102 spectrometer. ^{1}H NMR spectra were taken with a JEOL JNM-PMX 60SI NMR spectrometer for solutions in deuteriochloroform with TMS as internal standard. Mass spectra were obtained with a Hitachi M-2000 spectrometer. Elemental analyses were

Table 1. UV and Visible Spectra Data[a)]

Product	λ_{max} / nm	ε	Product	λ_{max} / nm	ε
7	666	50900	**17**	559	12500
	611	21200		529	11000
	421	13000		371	9800
	249	45900		348	9000
				277	18500
8	664	26100			
	610	11700	**19**	489	10100
	441	3000		318	12600
	347	3900		275	18500
	250	22200		258	21100
9	665	28800	**20**	489	24400
	611	13000		350	16400
	446	3300		317	19000
	347	4300		279	30200
	249	25300		256	34300
14	469	26100	**21**	573	19700
	360	19100		337	20900
	291	41000		281	40100
	273	43700			
			23	556	16800
16	475	11900		341	15900
	366	8100		279	34100
	291	23000		275	24800
	268	22400			

a) In chloroform.

performed by the Microanalytical Laboratory of Kyoto University.

Preparation of 2,6-Dichloro- and 2-Chloro-4,8-bis(2-propylamino)-1,5-naphthoquinone (3 and 5). To a solution of 4,8-bis(2-propylamino)-1,5-naphthoquinone[6] (**1**) (400 mg, 1.47 mmol) in 27% hydrochloric acid (30 ml) was added bromine (0.30 ml, 5.82 mmol) in 27% hydrochloric acid (10 ml) at 0 °C slowly over 2 h. After stirring for 30 min, the mixture was neutralized with a 5% aqueous $NaHCO_3$ solution, thereby the dark-brown color of the solution turned to blue. The solution was extracted with chloroform (3×15 ml). The combined extracts were washed successively with water (2×5 ml) and brine (2×5 ml). The solution was dried over $MgSO_4$ and evaporated. Column chromatography on silica gel with chloroform–ethyl acetate (9:1) as eluent yielded dichloronaphthoquinone **3** (226 mg, 45%) and chloronaphthoquinone **5** (117 mg, 26%).

3: Mp 200—210 °C (decomp) (from hexane–CH_2Cl_2); IR (KBr) 1593 and 1558 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (12H, d, J=6.0 Hz), 3.71—4.40 (2H, m), 7.46 (2H, s), and 12.78—13.14 (2H, m); MS m/z 342 (M^+; 47), 340 (M^+; 63), 338 (M^+; 11), 327 (61), 325 (100), and 323 (33). Found: C, 56.12; H, 5.08%. Calcd for $C_{16}H_{18}Cl_2N_2O_2$: C, 56.32; H, 5.32%.

5: Mp 145—150 °C (decomp) (from hexane–CH_2Cl_2); IR (KBr) 1598 and 1542 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (12H, d, J=6.0 Hz), 3.88—4.42 (2H, m), 7.00 (1H, d, J=10.0 Hz), 7.24 (1H, d, J=10.0 Hz), 7.45 (1H, s), and 12.45—13.46 (2H, m); MS m/z 307 (M^+; 28), 305 (M^+; 62), 291 (42), and 289 (100). Found: C, 62.65; H, 6.32%. Calcd for $C_{16}H_{19}ClN_2O_2$: C, 62.64; H, 6.24%.

Preparation of 2,6-Dichloro- and 2-Chloro-4,8-bis(methylamino)-1,5-naphthoquinone (4 and 6). Chlorination of 4,8-bis(methylamino)-1,5-naphthoquinone[6] (**2**) (300 mg, 1.39 mmol) with bromine (0.20 ml, 3.88 mmol) in 27% hydrochloric acid (10 ml) afforded **4** (87 mg, 22%) and **6** (125 mg, 36%).

4: Mp 220—230 °C (decomp) (from hexane–CH_2Cl_2); IR (KBr) 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.24 (6H, d, J=6.0 Hz), 7.51 (2H, s), and 12.63—12.86 (2H, m); MS m/z 286 (M^+; 41), 284 (M^+; 87), 282 (M^+; 58), and 207 (100). Found: C, 50.14; H, 3.47%. Calcd for $C_{12}H_{10}Cl_2N_2O_2$: C, 50.55; H, 3.54%.

6: Mp 190—200 °C (decomp) (from hexane–CH_2Cl_2); IR (KBr) 1595 and 1532 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.17 (3H, d, J=6.0 Hz), 3.24 (3H, d, J=6.0 Hz), 6.92 (1H, d, J=10.0 Hz), 7.18 (1H, d, J=10.0 Hz), 7.37 (1H, s), and 12.07—13.30 (2H, m); MS m/z 252 (M^+; 37), 250 (M^+; 100), 235 (17), and 233 (42). Found: C, 57.39; H, 4.28%. Calcd for $C_{12}H_{11}ClN_2O_2$: C, 57.50; H, 4.42%.

Selenation of 2,6-Dichloro-4,8-bis(2-propylamino)-1,5-naphthoquinone (3). A solution of diphenyl diselenide (68 mg, 0.22 mmol) and tributylphosphine (60 µl, 0.24 mmol) in THF (0.5 ml) was vigorously stirred ultrasonically under argon atmosphere at room temperature for 5 min. To this was added a 10% aqueous NaOH solution (160 µl, 0.44 mmol), and the mixture was ultrasonically stirred further for 15 min, during which time the two-phase mixture became homogeneous and the starting yellow solution turned to colorless. Then, the mixture was added dropwise to a solution of **3** (68 mg, 0.20 mmol) in THF (0.5 ml) at room temperature under argon atmosphere and stirred for 15 min. The mixture was then poured into a mixture of brine (10 ml) and dichloromethane (10 ml), and the aqueous layer was extracted with dichloromethane (2×5 ml). The combined extracts were washed with brine (5 ml), dried over $MgSO_4$, and evaporated. Column chromatography on silica gel with hexane–ethyl acetate (7:3) as eluent yielded 4,8-bis(2-propylamino)-2,6-bis(phenylseleno)-1,5-naphthoquinone (**7**) (102 mg, 88%). Mp 220—223 °C (from hexane–CH_2Cl_2); IR (KBr) 1585 and 1532 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.12 (12H, d, J=6.0 Hz), 3.09—3.74 (2H, m), 6.39 (2H, s), 7.21—7.83 (10H, m), and 12.33—12.60 (2H, m); MS m/z 584 (M^+; 35), 582 (M^+; 33), 580 (M^+; 15), 427 (94), 425 (45), 411 (100), and 409 (53). Found: C, 58.02; H, 4.76%. Calcd for $C_{28}H_{28}N_2O_2Se_2$: C, 57.74; H, 4.85%.

Selenation of 2-Chloro-4,8-bis(2-propylamino)-1,5-naphthoquinone (5). Selenation of **5** (61 mg 0.20 mmol) using diphenyl diselenide (34 mg, 0.11 mmol), tributyphosphine (30 µl, 0.12 mmol), and a 10% aqueous NaOH solution (80 µl, 0.22 mmol) gave 4,8-bis(2-propylamino)-2-phenylseleno-1,5-naphthoquinone (**8**) (80 mg, 94%). Mp 141—143 °C (from hexane–CH_2Cl_2); IR (KBr) 1588 and 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.12 (6H, d, J=6.0 Hz), 1.38 (6H, d, J=6.0 Hz), 3.05—3.77 (1H, m), 3.77—4.30 (1H, m), 6.46 (1H, s), 6.98—7.33 (2H, m), 7.33—7.78 (5H, m), and 12.37—12.98 (2H, m); MS m/z 428 (M^+; 100), 426 (M^+; 56), 411 (43), 409 (20), 272 (34), and 270 (15). Found: C, 61.80; H, 5.71%. Calcd for $C_{22}H_{24}H_2O_2Se$: C, 61.82; H, 5.67%.

Selenation of 2-Chloro-4,8-bis(methylamino)-1,5-naphthoquinone (6). Selenation of **6** (50 mg 0.20 mmol) using diphenyl diselenide (34 mg, 0.11 mmol), tributylphosphine (30 µl, 0.12 mmol), and a 10% aqueous NaOH solution (80 µl, 0.22 mmol) gave 4,8-bis(methylamino)-2-phenylseleno-1,5-naphthoquinone (**9**) (66 mg, 89%). Mp 185—187 °C (from hexane–CH_2Cl_2); IR (KBr) 1583 and 1544 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.63 (3H, d, J=5.4 Hz), 3.30 (3H, d, J=5.4 Hz), 6.51 (1H, s), 7.01—7.35 (2H, m), 7.35—7.82 (5H, m), and 12.27—12.93 (2H, m); MS m/z 372 (M^+; 100) and 370 (M^+; 56). Found: C, 57.98; H, 4.20%. Calcd for $C_{18}H_{16}N_2O_2Se$: C, 58.23; H, 4.34%.

Preparation of Bis(3-amino-2-pyridyl) diselenide (12). A solution of 2-chloro-3-nitropyridine (**10**) (5.0 g, 31.5 mmol) and potassium selenocyanate (7.5 g, 52.1 mmol) in DMF (40 ml) were heated at 120 °C for 8 h. To this was added a 10% aqueous NaOH solution (100 ml, 277.5 mmol). After stirring for 2 h at room temperature, the mixture was poured into water to form precipitates, which were filtered. The precipitates were dissolved in acetic acid (250 ml), and to this solution was added powder zinc (10.0 g, 153.0 mmol) at 60 °C. The mixture was stirred for 40 min at the same temperature. A 20% hydrochloric acid (80 ml) was then and stirred for 10 min. The mixture was filtered and the filtrate was neutralized with a 5% aqueous $NaHCO_3$ solution to form precipitates, which were filtered, washed with water, and dried under reduced pressure. Recrystallization from EtOH gave **12** (2.88 g, 53%). Mp 193—195 °C (from $CHCl_3$); IR (KBr) 3420 and 3260 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.60—5.85 (4H, m), 6.83—7.20 (4H, m), and 7.60—7.83 (2H, m); MS m/z 346 (M^+; 100) and 344 (M^+; 91). Found: C, 34.81; H, 2.74; N, 16.46%. Calcd for $C_{10}H_{10}N_4Se_2$: C, 34.90; H, 2.93; N, 16.28%.

Preparation of 6-Methyl-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*]-[1,4]selenazin-5-one (14). Method A: solution of **12** (25 mg, 0.07 mmol) and triphenylphosphine (40 mg, 0.15 mmol) in acetonitrile (3 ml) was ultrasonically stirred under argon atmosphere at room temperature for 5 min. To this was added a 5% aqueous NaOH solution (100 µl, 0.13 mmol) and stirred for 15 min. Then, 2-bromo-3-methyl-1,4-naphthoquinone

(**13**) (30 mg, 0.12 mmol) was added and stirred for 40 min. The mixture was poured into a water (20 ml) to form precipitates, which were filtered washed with water (10 ml), dried under reduced pressure. Column chromatography on silica gel with toluene–ethyl acetate (8:2) as eluent yielded **14** (36 mg, 91%).

Method B: The reaction of **13** (30 mg, 0.12 mmol) with 3-amino-2-pyridineselenolate ion generated from **12** using tributylphosphite (38 μl, 0.15 mmol) gave **14** (37 mg, 93%). Mp 237—238 °C (from benzene); IR (KBr) 1620 cm^{-1}; ^1H NMR (DMSO-d_6, 90 °C) δ=2.10 (3H, s), 7.54—7.66 (1H, m), 7.76—7.92 (2H, m), 8.14—8.30 (2H, m), 8.51—8.60 (1H, m), and 8.72—8.82 (1H, m); MS *m/z* 326 (M^+; 100) and 324 (M^+; 56). Found: C, 59.34; H, 3.10; N, 8.51%. Calcd for $C_{16}H_{10}N_2OSe$: C, 59.09; H, 3.10; N, 8.61%.

Reaction of 2,3-Dichloro-1,4-naphthoquinone (15) with 3-Amino-2-pyridineselenolate Ion Generated from 12. Method A: The reaction of **15** (30 mg, 0.13 mmol) with selenolate ion generated from **12** (30 mg, 0.09 mmol), triphenylphosphine (50 mg, 0.19 mmol), and a 5% aqueous NaOH solution (112 μl, 0.15 mmol), gave 6-chloro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*]-[1,4]selenazin-5-one (**16**) (28 mg, 61%) and pyrido[2,3-*b*]-pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*][1,4]selenazine (**17**) (11 mg, 18%).

Method B: The reaction of **15** (30 mg, 0.13 mmol) with 3-amino-2-pyridineselenolate ion generated from **12** using tributylphosphine (48 μl, 0.19 mmol) gave **16** (9 mg, 20%) and **17** (33 mg, 54%).

16: Mp 282—285 °C (from benzene); IR (KBr) 1628 cm^{-1}; ^1H NMR (DMSO-d_6, 90 °C) δ=7.64—7.72 (1H, m), 7.87—7.99 (2H, m), 8.22—8.33 (1H, m), 8.36—8.45 (1H, m), 8.62—8.68 (1H, m), and 8.84—8.91 (1H, m); MS *m/z* 348 (M^+; 42), 346 (M^+; 100), and 344 (M^+; 50). Found: C, 52.40; H, 1.99; N, 8.18%. Calcd for $C_{15}H_7ClN_2OSe$: C, 52.12; H, 2.04; N, 8.10%.

17: Mp 280—281 °C (from EtOH); IR (KBr) 1562 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.36—7.46 (2H, m), 7.74—7.82 (2H, m), 8.04—8.14 (2H, m), 8.43—8.50 (2H, m), and 8.88—8.99 (2H, m); MS *m/z* 466 (M^+; 100) and 464 (M^+; 96). Found: C, 51.80; H, 2.08; N 11,85%. Calcd for $C_{20}H_{10}N_4Se_2$: C, 51.74%; H, 2.17; N, 12.07%.

Reaction of 2,3-Dichloro-5-nitro-1,4-naphthoqionone[7] (18) with 3-Amino-2-pyridineselenolate Ion Generated from 12. Method A: The reaction of **18** (60 mg, 0.22 mmol) with selenolate ion generated from **12** (50 mg, 0.15 mmol), triphenylposphine (84 mg, 0.32 mmol), and a 5% aqueous NaOH solution (190 μl, 0.25 mmol), gave 6-chloro-1-nitro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]selenazin-5-one (**19**) (40 mg, 47%), 6-chloro-4-nitro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]-selenazin-5-one (20) (16 mg, 19%), and 6-nitropyrido[2,3-*b*]-pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*]-[1,4]selenazine (**21**) (19 mg, 17%).

Method B: The reaction of **18** (60 mg, 0.22 mmol) with 3-amino-2-pyridineselenolate ion generated from **12** using tributylphosphine (80 μl, 0.32 mmol) gave **19** (26 mg, 30%), **20** (15 mg, 18%), and **21** (45 mg, 40%).

19: Mp 277 °C (from EtOH); IR (KBr) 1635, 1523, and 1372 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.56—7.68 (1H, m), 7.84—8.11 (3H, m), 8.36—8.44 (1H, m), and 8.50—8.66 (1H, m); MS *m/z* 393 (M^+; 40), 391 (M^+; 100), nad 389 (M^+; 47). Found: C, 46.28; H, 1.51; N, 10.82%. Calcd for $C_{15}H_6ClN_3O_3Se$: C, 46.12; H, 1.55; N, 10.76%.

20: Mp 313 °C (from EtOH); IR (KBr) 1620, 1522, and 1362 cm^{-1}; ^1H NMR (DMSO-d_6, 90 °C) δ=7.70—7.80 (1H, m), 8.09—8.16 (2H, m), 8.44—8.52 (1H, m), 8.68—8.74 (1H, m), and 9.08—9.16 (1H, m); MS *m/z* 393 (M^+; 45), 391 (M^+; 100), and 389 (M^+; 47). Found: C, 46.09; H, 1.48; N, 10.71%. Calcd for $C_{15}H_6ClN_3O_3Se$: C, 46.12; H, 1.55; N, 10.76%.

21: Mp 332 °C (from benzene); IR (KBr) 1514 and 1352 cm^{-1}; ^1H NMR (DMSO-d_6, 90 °C) δ=7.39—7.53 (1H, m), 7.74—7.82 (1H, m), 7.86—8.00 (2H, m), 8.08—8.18 (1H, m), 8.42—8.52 (2H, m), and 9.02—9.10 (1H, m); MS *m/z* 511 (M^+; 100) and 509 (M^+; 89). Found: C, 47.18; H, 1.70; N, 13.50%. Calcd for $C_{20}H_9N_5O_2Se_2$: C, 47.17; H, 1.78; N, 13.75%.

Condensation of 6-Chloro-1-nitro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]selenazin-5-one (19) with 2-Aminobenzenethiol (22). A mixture of **22** (16 mg, 0.13 mmol), Na_2CO_3 (28 mg, 0.26 mmol), and **19** (40 mg, 0.10 mmol) in DMF (1 ml) and toluene (1 ml) was heated at 120 °C for 6 h. The mixture was poured into water (20 ml) to form precipitates, which were filtered, washed with water (10 ml), and dried under reduced pressure. Column chromatography on silica gel with toluene–ethyl acetate (8:2) as eluent yielded 6-nitrobenzo[*b*]pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]naphtho[1,2-*e*][1,4]thiazine (**23**) (26 mg, 57%). Mp 308—309 °C (from benzene); IR (KBr) 1530 and 1377 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.40—7.54 (3H, m), 7.68—7.90 (5H, m), 8.33—8.44 (1H, m), and 9.10—9.19 (1H, m); MS *m/z* 462 (M^+; 79), 460 (M^+; 43), 430 (100), and 428 (55). Found: C, 54.84; H, 2.11; N, 11.91%. Calcd for $C_{21}H_{10}N_4O_2SSe$: C, 54.67; H, 2.18; N, 12.14%.

Condensation of 6-Chloro-4-nitro-5*H*-naphtho[2,1-*b*]pyrido[3,2-*e*][1,4]selenazin-5-one (20) with 22. The condensation of **20** (15 mg, 0.04 mmol) carried out as above using **22** (6 mg, 0.05 mmol), Na_2CO_3 (11 mg, 0.10 mmol) yielded 9-nitrobenzo[*b*]pyrido[3″,2″:5′,6′][1,4]selenazino[2′,3′:3,4]-naphtho[1,2-*e*][1,4]thiazine (**25**) (15 mg, 81%). Mp 337—339 °C (from benzene); IR (KBr) 1532 and 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.37—7.47 (2H, m), 7.52—7.60 (2H, m), 7.69—7.79 (3H, m), 7.96—8.03 (1H, m), 8.39—8.43 (1H, m), and 9.09—9.16 (1H, m); MS *m/z* 462 (M^+; 100), 460 (M^+; 52), 430 (53), and 428 (25). Found: C, 54.41; H, 2.58; N, 11.71%. Calcd for $C_{21}H_{10}N_4O_2SSe$: C, 54.67; H, 2.18; N, 12.14%.

Reaction of 6-Chloro-4-nitro-5*H*-benzo[*a*]phenothiazin-5-one (24) with 3-Amino-2-pyridineselenolate Ion Generated from 12. To a mixture containing 3-amino-2-pyridineselenolate ion generated from **12** (20 mg, 0.06 mmol), tributylphosphine (30 μl, 0.12 mmol), and a 5% aqueous NaOH solution (76 μl, 0.10 mmol) as described in the preparation of **14** was added a solution of **24** (30 mg, 0.09 mmol) in DMSO (1 ml). The mixture was heated at 160 °C for 4 h. The mixture was poured into a water (20 ml) to form precipitates, which were filtered, washed with water (10 ml), and dried under pressure. Column chromatography on silica gel with toluene as eluent yielded **23** (13 mg, 32%).

Reaction of 6-Chloro-1-nitro-5*H*-benzo[*a*]phenothiazin-5-one (26) with 3-Amino-2-pyridineselenolate Ion Generated from 12. The reaction of **26** (30 mg, 0.09 mmol) with 3-amino-2-pyridineselenolate ion generated from **12** (20 mg, 0.06 mmol), tributylphosphine (30 μl, 0.12 mmol), and a 5% aqueous NaOH solution (76 μl. 0.10 mmol) gave **25** (22 mg, 52%).

Crystallographic Study. A crystal was obtained by slow crystallization from CH_2Cl_2–hexane. A Rigaku automated four-circle diffractometer AFC-5R was used with graphite monochromated Cu radiation (CuK=1.5418 Å).

Table 2. Final Position Parameters and B_{eq} in Crystal Structure of 7[a)]

Atom	x/a	y/b	z/c	B_{eq}/Å^2
C1	0.1176(8)	−0.0604(7)	−0.2441(8)	3.6(2)
C2	0.2011(9)	−0.1499(8)	−0.282(1)	4.5(3)
C3	−0.068(1)	−0.2864(9)	−0.535(1)	5.4(3)
C4	0.106(1)	−0.2610(9)	−0.427(1)	5.2(3)
C5	−0.151(1)	−0.1957(9)	−0.495(1)	5.0(3)
C6	−0.0581(8)	−0.0839(7)	−0.3486(9)	3.9(2)
C7	0.4432(8)	0.1239(6)	0.3271(8)	3.1(2)
C8	0.3396(8)	0.0210(7)	0.1626(8)	3.6(2)
C9	0.3046(8)	−0.1214(7)	0.1569(8)	3.2(2)
C10	0.3795(7)	−0.1728(6)	0.3295(8)	3.0(2)
C11	0.4845(8)	−0.0736(6)	0.5013(8)	2.9(2)
C12	0.2580(9)	−0.4235(7)	0.167(1)	4.0(2)
C13	0.195(1)	−0.5538(8)	0.225(1)	5.1(3)
C14	0.372(1)	−0.449(1)	0.093(1)	6.1(3)
N1	0.3506(7)	−0.3104(5)	0.3291(7)	3.5(2)
O1	0.4680(6)	0.2528(4)	0.3157(5)	4.0(2)
Se1	0.2482(1)	0.10442(8)	−0.0532(1)	4.20(3)

a) Atoms are labeled as shown in Fig. 1. Estimated standard deviations, in parentheses, occur in the last figures for each parameter. $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \boldsymbol{a}_i \boldsymbol{a}_j$.

Table 3. Selected Bond Lengths and Bond Angles for 7[a)]

	Bond lengths (Å)		
C8–C7	1.417(8)	C11–C11	1.43(1)
C9–C8	1.373(9)	N1–C10	1.331(8)
C9–H1	0.96(4)	N1–C12	1.460(7)
C10–C9	1.488(8)	O1–C7	1.267(7)
C11–C7	1.435(8)	Se1–C1	1.920(6)
C11–C10	1.438(7)	Se1–C8	1.911(6)
	Bond angles (deg)		
C6–C1–C2	120.9(6)	C10–C9–H1	120(3)
Se1–C1–C2	120.2(5)	C11–C10–C9	119.2(5)
Se1–C1–C6	118.8(5)	N1–C10–C9	120.4(5)
C11–C7–C8	116.8(6)	N1–C10–C11	120.4(5)
O1–C7–C8	119.3(5)	C10–C11–C7	119.4(5)
O1–C7–C11	123.9(5)	C11–C11–C7	121.0(6)
C9–C8–C7	124.7(60	C11–C11–C10	119.5(7)
Se1–C8–C7	111.8(5)	C10–N1–C12	126.7(5)
Se1–C8–C9	123.5(4)	C10–N1–H2	112(4)
C8–C9–H1	120(3)	C12–N1–H2	119(4)
C10–C9–C8	118.7(5)	C1–Se1–C8	100.7(3)

a) Labeling corresponds to that indicated in Fig. 1. Estimated standard deviations in parentheses.

$C_{28}H_{28}N_2O_2Se_2$, M_r=582.46; triclinic, $P\bar{1}$,
a=9.273 (1) Å, b=9.849 (1) Å, c=8.468 (1) Å,
α=93.90 (1)°, β=119.83°, γ=100.64 (1)°,
V=647.7 (1) Å^3, D_C=1.493 g cm^{-3};
Crystal size, 0.10×0.20×0.30 mm;
2081Intensities were collected, $2\theta_{max}$=126°.

Structures were solved with the aids of Texsan program system, and refined by the full-matrix least squares program using 1816 greater than $3\sigma(F)$. Non-H atoms were assigned anisotropic temperature factors. Hydrogen atoms were located from a difference Fourier map and refined with the equivalent isotropic temperature factor to that for the bonded carbon atoms.

$$R=0.057,\ R_W=[\sum_W(|F_o|^2-|F_c|^2)^2/\sum_W|F_o|^2]^{1/2}$$

$$W=1/\sigma^2(F^2),\ \Delta\rho_{max}=2.8/\text{e Å}^3.$$

Atomic scattering factors were employed from "International Table for X-Ray Crystallography". ORTEP was employed for drawing the molecular structures (Fig. 1). All calculations were made on a microVax 3500. Listing of atomic parameters, thermal parameters, selected bond lengths and bond angles are included in the supplementary material Tables 2 and 3.[9)]

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9) Tables of complete $|F_o-F_c|$ data, anisotropic thermal parameters, and coordinates of hydrogen atoms are deposited as Document No. 8946 at the Office of the Editor of Bull. Chem. Soc. Jpn.