New Selenenylation Method. Synthesis of Selenonaphthoquinones and Selenoquinolinequinones Mediated by Phenyl Selenide Ion

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Treatment of diphenyl diselenide and tributylphosphine with aqueous NaOH was found to be a good method for the generation of phenyl selenide ion. A variety of 2-halogeno-1,4-naphthoquinones and halogenoquinolinequinones were efficiently converted into the corresponding seleno compounds. Selenenylation of 2,3-dichloro-1,4-naphthoquinone gave 2,3-bis(phenylseleno)-1,4-naphthoquinone. The reaction of 2-bromo-1,4-napthoquinone afforded 2,3-bis(phenylseleno)naphthoquinone in significant yield, in addition to 2-(phenylseleno)naphthoquinone as a major product. Formation of the diseleno compound was minimized when the reaction was carried out under completely oxygen-free conditions. The reaction mechanism of this selenenylation is discussed.

In a previous report[1] we demonstrated that introduction of a phenylthio group at the 2-position caused a significant increase in the reactivity of the 1,4-naphthoquinone moiety towards Michael addition with lithium enolates or pyridinium ylides. We also demonstrated that the resulting 1,4-addition products were cyclized to a naphtho[2,3-*b*]furan ring-system *via* the elimination of the phenylthio group, and to naphtho[1,2-*b*]furans on acid treatment.[2] Continuing our work, we needed selenonaphthoquinones in order to study their reactivity towards Michael addition and their possible use as precursors for other selenium-containing heterocycles.

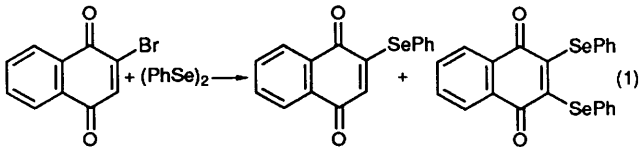
We herein report a new, efficient method for generation of phenyl selenide ion from diphenyl diselenide by treatment with tributylphosphine and aqueous alkali, and also describe the preparation of a number of selenoquinones such as 2-(phenylseleno)- and 2,3-bis(phenylseleno)-1,4-naphthoquinones and 2-(phenylseleno)quinolinequinones.

Results and Discussion

We first tried the selenenylation of 2-bromo-1,4-naphthoquinone[3] **1** according to known methods. Reaction of bromonaphthoquinone **1** with phenyl selenide ion, formed on treatment of diphenyl diselenide with sodium borohydride,[4] gave 2-(phenylseleno)-1,4-naphthoquinone **2** and 2,3-bis(phenylseleno)-1,4-naphthoquinone **3** in 32 and 2% yield, respectively. The selenenylated naphthoquinones **2** and **3** were obtained in similarly low yields when sodium metal[5] or dispersed sodium[6,†] was used in place of sodium borohydride. We therefore searched for a better method for the preparation of selenonaphthoquinones.

Several methods for selenenylation of hydroxy groups have been reported. Primary or secondary alcohols are converted into selenides by treatment with phosphine and an aryl selenocyanate[7] or an *N*-(arylseleno)phthalimide.[8] In these reactions an aryl selenide ion is liberated as an alkoxyphosphonium ion is formed. The liberation of phenyl selenide ion from diphenyl diselenide instead of the activated selenocyanate and selenophthalimide may be rather difficult. Conversion of a hydroxy group of a phosphoric ester into a seleno group by treatment with diphenyl diselenide and tributylphosphine has been reported but the yield was low.[9] We studied the formation of phenyl selenide ion from diphenyl diselenide by use of hydroxide ion instead of the organic hydroxy group and found that this system could efficiently generate the phenyl selenide ion. We examined the formation of selenonaphthoquinones by using diphenyl diselenide, tributylphosphine, and aq. alkali under various reaction conditions.

In a typical experiment (entry 1 in Table 1), a tetrahydrofuran (THF) solution of diphenyl diselenide (0.55 mol equiv.) and tributylphosphine (0.60 mol equiv.) was vigorously stirred under argon at room temperature. To this was added aq. NaOH (1.10 mol equiv.). The mixture was vigorously stirred for 15 min during which time the yellow, two-phase solution became colourless and homogeneous. The mixture was then added dropwise to a solution of 2-bromonaphthoquinone in THF. Purification by column chromatography furnished 2-(phenylseleno)-1,4-naphthoquinone **2** and 2,3-bis(phenylseleno)-1,4-naphthoquinone **3** in 73 and 12% yield, respectively [eqn. (1)].



1 **2** **3**

Reagents and conditions: Bu_3P, aq. NaOH, THF, room temp.

Reaction Mechanism.—Triphenyl(phenylthio)phosphonium ion **4** has been proposed[10] as the intermediate in the reduction of diphenyl disulphide into thiophenol by the action of phosphine and water. Analogously the reaction mechanism shown in Scheme 1 can be postulated to occur in our reaction. Initially, a selenophosphonium ion **5** and/or a pentavalent phosphorus species **6** may be formed. Addition of NaOH liberates sodium selenide and the phosphonium ion **7**, from which is generated more sodium selenide together with phosphine oxide by the action of NaOH. Consequently, overall, 2 moles of phenyl selenide ion are formed from 1 mole of diphenyl diselenide, while 2 moles of NaOH and 1 mole of tributylphosphine are consumed. This is in good accord with the experimental results obtained under several reaction conditions as shown in Table 1. The best yield of selenonaphthoquinone **2** was obtained in the reaction utilizing the reagents diphenyl diselenide, tributylphosphine and NaOH in the proportions 1:1:2.

† We obtained a slight increase in the yield of monoselenide **2** in the reaction with sodium phenyl selenide, prepared using dispersed sodium, by the addition of tributylphosphine oxide (0.60 molar equiv.) or water (excess), but the yield still remained low; 39 and 40% yield for phosphine oxide and water, respectively, compared with 30% for no additive.

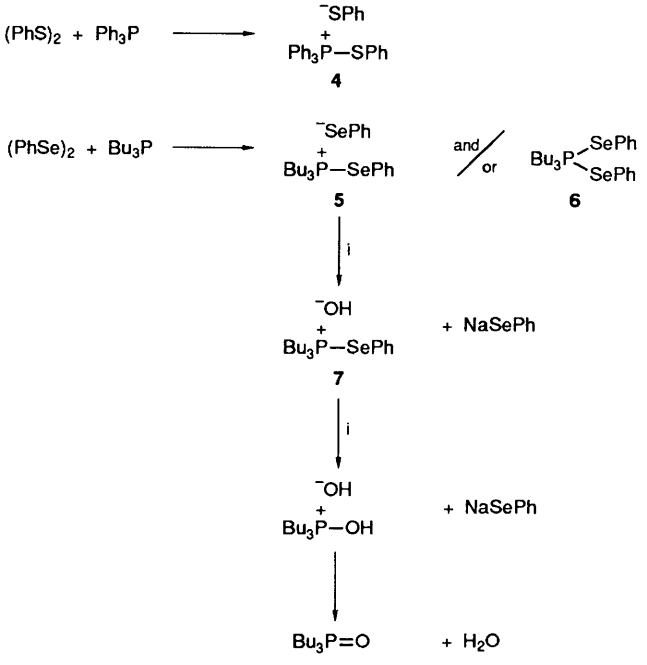
Table 1 Selenenylation of 2-bromo-1,4-naphthoquinone **1** under various reaction conditions, all at room temperature

Entry	$(PhSe)_2$ (mol equiv.)	Bu_3P (mol equiv.)	NaOH (mol equiv.)	Reaction time	Yield (%) **2**	Yield (%) **3**
1	0.55	0.60	1.10	10 min	73	12[c]
2	0.55	0.60	1.10	10 min[a]	84	0[c]
3	0.55	0.60		1 h	1[b]	1[d]
4	0.55	0.60	0.55	2.5 h	43	4[e]
5	0.55	0.60	2.20	10 min	17	0[c]
6	0.55		3.35	4 h	2	0[c]
7	0.55	1.10	1.10	10 min	42	1[c]

[a] The reaction was carried out under completely oxygen-free conditions. [b] 2-Bromo-3-(phenylseleno)-1,4-naphthoquinone **11** was isolated in 4% yield. [c] Starting bromonaphthoquinone **1** was completely consumed. [d] Compound **1** was recovered in 55% yield. [e] Compound **1** was recovered in 21% yield.

Table 2 Selenenylation of 1,4-naphthoquinones **11** and **12**

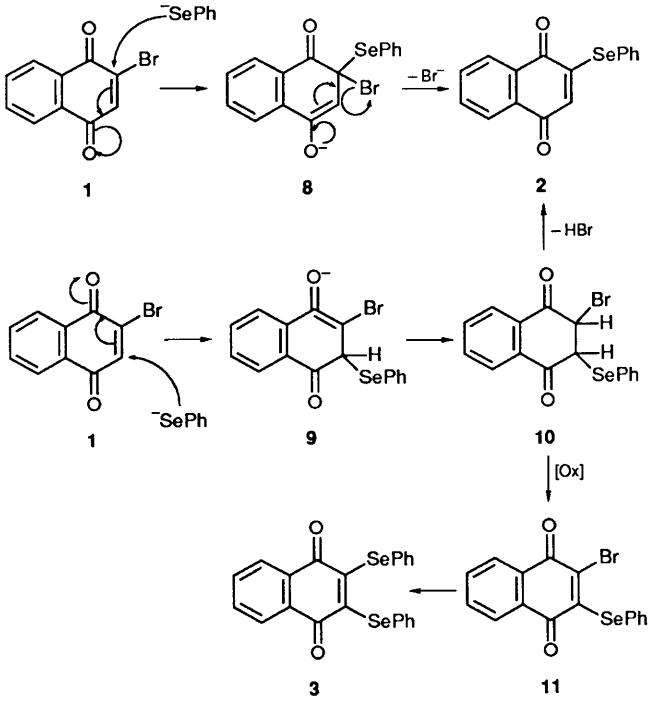
Substrate	X	Y	Time (*t*/min)	Product	Yield (%)
12a	Br	Me	10	**13a**	90
12b	Cl	OMe	15	**13b**	96
12c	Cl	OEt	15	**13c**	93
12d	Cl	NMe_2	10	**13d**	98
12e	Cl	N(Ac)Me	30	**13e**	68
12f	Br	SEt	15	**13f**	91
12g	Cl	SePh	15	**3**	89
11	Br	SePh	10	**3**	89
12h	Cl	Cl	15	**3**	83



Scheme 1 *Reagent:* i, NaOH

It is known that a phenyl selenide ion or a phenyl sulphide ion is formed from the corresponding diphenyl diselenide or diphenyl disulphide by the action of alkali metal hydroxide.[11] However, this would not be the case in the present reaction, since the reaction of bromide **1** without tributylphosphine, *i.e.*, the reaction with diphenyl diselenide and NaOH, gave only a trace amount (2%, entry 6 in Table 1) of monoselenide **2** while the starting bromonaphthoquinone **1** was completely consumed. In addition, when a greater excess of NaOH was used, together with tributylphosphine, the yield of monoselenide **2** decreased considerably (entry 5). These results show that the amount of NaOH is crucial and a 2-fold excess of NaOH should be used, since the excess of NaOH may decompose the naphthoquinone moiety of reactant **1** and/or product **2**, lowering the yield of product **2**. A large excess of tributylphosphine also decreases the yield of the selenide **2** (entry 7).

Attack of phenyl selenide ion thus formed may occur on either of the carbon atoms at the 2- and the 3-position of 2-bromonaphthoquinone **1** to afford 2-(phenylseleno)naphthoquinone **2** as shown in Scheme 2. Cameron has shown, using 2-chloro-1,4-[2-^{13}C]naphthoquinone, that the attack of soft nucleophiles occurs at both the 2- and the 3-position.[12]



Scheme 2

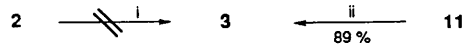
As for the formation of 2,3-bis(phenylseleno)naphthoquinone **3**, it was found that the diseleno compound **3** was not formed simply by further selenenylation of the first produced selenonaphthoquinone **2**. No formation of diselenide **3** was observed in the reaction of the isolated selenonaphthoquinone **2** with phenyl selenide ion generated in the usual manner. In contrast, diselenonaphthoquinone **3** was formed in 89% yield in the reaction of 2-bromo-3-(phenylseleno)naphthoquinone **11** with phenyl selenide ion generated from diphenyl diselenide, tributylphosphine, and NaOH under conditions similar to those of the typical procedure. Hence, in the reaction of 2-bromonaphthoquinone **1** the attack of phenyl selenide ion occurs at the 3-position to form an enolate **9**, which (after protonation) presumably equilibrates with the quinone **10**.

Table 3 Physical, ^{1}H NMR, IR and MS spectroscopic data of selenonaphthoquinones

Selenonaphthoquinone (Formula)	M.p.[a] (°C)	^{1}H NMR δ($CDCl_3$)	IR (ν_{max}/cm^{-1})	MS (*m*/*z*)
2 ($C_{16}H_{10}O_2Se$)	153.5–154.8	6.33 (1 H, s), 7.30–7.87 (7 H, m), 7.87–8.22 (2 H, m)	1662, 1647, 1587, 1558	314 (M^+, 100%), 312 (M^+, 53), 286 (54), 270 (32), 258 (26), 157 (19)
3 ($C_{22}H_{14}O_2Se_2$)	153.2–155.0	6.97–7.33 (6 H, m), 7.33–7.73 (6 H, m), 7.73–8.07 (2 H, m)	1650, 1585	470 (M^+, 91%), 468 (M^+, 79), 466 (M^+, 53), 313 (100), 285 (33), 256 (37)
13a ($C_{17}H_{12}O_2Se$)	104.0–105.0	2.16 (3 H, s), 7.08–7.34 (3 H, m), 7.34–7.79 (4 H, m), 7.79–8.10 (2 H, m)	1662, 1650, 1587, 1560	328 (M^+, 100%), 326 (M^+, 54), 313 (14), 171 (44), 143 (23), 115 (82)
13b ($C_{17}H_{12}O_3Se$)	82.3–83.0	3.73 (3 H, s), 7.12–7.40 (3 H, m), 7.46–7.82 (4 H, m), 7.92–8.20 (2 H, m)	1652, 1587, 1560	344 (M^+, 100%), 342 (M^+, 52), 313 (14), 267 (16), 187 (18), 157 (25)
13c ($C_{18}H_{14}O_3Se$)	86.7–87.5	1.05 (3 H, t, *J* 7.0 Hz), 4.21 (2 H, q, *J* 7.0 Hz), 7.05–7.34 (3 H, m), 7.34–7.76 (4 H, m), 7.76–8.11 (2 H, m)	1647, 1583, 1558	358 (M^+, 100%), 356 (M^+, 50), 201 (77), 186 (40), 157 (50)
13d[b] ($C_{18}H_{15}NO_2Se$)		2.92 (6 H, s), 7.08–7.50 (5 H, m), 7.78 (2 H, m), 7.78–8.17 (2 H, m)	1655, 1623, 1585, 1528[c]	357 (M^+, 100%), 355 (M^+, 50), 200 (50)
13e ($C_{19}H_{15}NO_3Se$)	145.8–147.0	1.72 (3 H, s), 2.77 (3 H, s), 7.24–7.48 (3 H, m), 7.48–7.82 (4 H, m), 7.98–8.21 (2 H, m)	1654, 1585, 1556	385 (M^+, 1.3%), 383 (M^+, 0.4), 342 (5), 314 (3), 228 (100), 185 (49), 169 (28), 157 (26), 128 (26)
13f ($C_{18}H_{14}O_2SSe$)	74.8–76.0	1.28 (3 H, t, *J* 7.0 Hz), 3.25 (2 H, q, *J* 7.0 Hz), 7.12–7.39 (3 H, m), 7.39–7.83 (4 H, m), 7.83–8.12 (2 H, m)	1651, 1583	374 (M^+, 100%), 372 (M^+, 51), 359 (11), 345 (18), 313 (10), 297 (29), 281 (28), 265 (25), 217 (16), 189 (48), 157 (33)
12g ($C_{16}H_9ClO_2Se$)	131.7–133.5	7.24–7.41 (3 H, m), 7.41–7.77 (4 H, m), 7.86–8.23 (2 H, m)	1665, 1583	350 (M^+, 45%), 348 (M^+, 100), 346 (M^+, 49), 313 (69), 285 (18), 193 (5), 165 (22), 137 (11)
11 ($C_{16}H_9BrO_2Se$)	159.2–161.0	7.20–7.47 (3 H, m), 7.47–7.82 (4 H, m), 7.82–8.03 (1 H, m), 8.03–8.23 (1 H, m)	1657, 1578	394 (M^+, 80%), 392 (M^+, 100), 390 (M^+, 57), 313 (70), 285 (30), 237 (20), 209 (30), 181 (43)
15a ($C_{15}H_9NO_2Se$)	197.8–199.1	6.52 (1 H, s), 7.28–7.78 (6 H, m), 8.30–8.54 (1 H, m), 8.88–9.10 (1 H, m)	1657, 1572, 1548	315 (M^+, 84%), 313 (M^+, 50), 286 (28), 258 (69), 238 (9), 182 (16), 157 (17), 130 (9), 102 (100)
15b ($C_{15}H_9NO_2Se$)	158.9–161.0	6.38 (1 H, s), 7.24–7.73 (6 H, m), 8.17–8.39 (1 H, m), 8.84–9.06 (1 H, m)	1667, 1647, 1574, 1557	315 (M^+, 76%), 313 (M^+, 40), 286 (22), 258 (51), 238 (6), 182 (8), 157 (14), 130 (16), 102 (100)

[a] From hexane–methylene dichloride. [b] Violet oil. [c] On film.

Compound **10** is then oxidized to bromo(seleno)naphthoquinone **11**. Diselenonaphthoquinone **3** is then produced as described above, by attack of phenyl selenide ion on the C-2 carbon of compound **11**. The intermediate quinone **10** is oxidized probably by oxygen dissolved in the solution. In fact, selenenylation in a completely oxygen-free solution was found



Reagents and conditions: i, $(PhSe)_2$, Bu_3P, aq. NaOH, THF, room temp., overnight; ii, as for i, but for 10 min

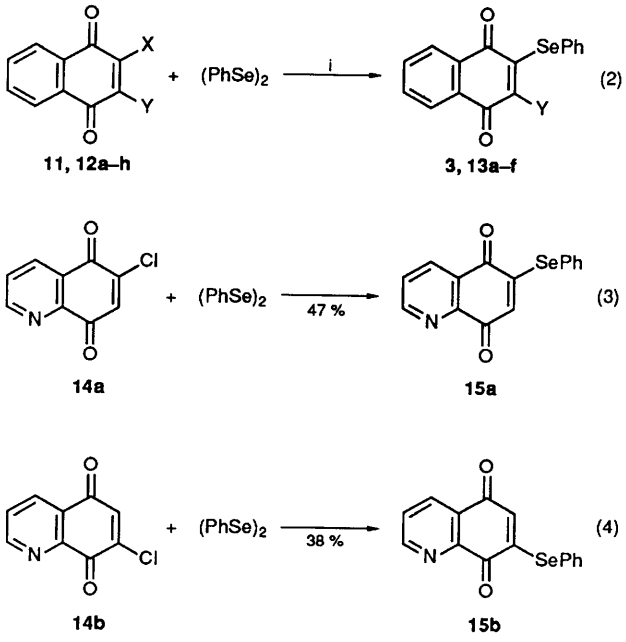
to give a better yield of monoselenide **2** and to suppress substantially the formation of compound **3**, when compared with the results obtained in the reaction simply carried out under argon but without any special precautions taken to degas the solution completely (entries 1 and 2 in Table 1).

Consequently, the attack of phenyl selenide ion occurs at both the 2- and the 3-position of 2-bromonaphthoquinone **1**. Diselenonaphthoquinone **3** is formed *via* the bromo(seleno)-naphthoquinone **11** produced by attack at the 3-position. This process involves oxidation, and thus, without oxygen, the quinone **10** may not react further but will reversibly afford the starting bromonaphthoquinone **1** *via* the enolate **9**, or yield selenonaphthoquinone **2** directly.

Selenenylation of Substituted 1,4-*Naphthoquinones.*—Table 2 shows the results of selenenylation of various 2-halogeno- or 2,3-dihalogeno-1,4-naphthoquinones. 2-Chloro-or 2-bromo-1,4-naphthoquinones **12a–e** carrying a substituent such as methyl,[13] methoxy,[14] ethoxy,[14] dimethylamino,[15] or *N*-methylacetamido[16] at the 3-position gave 2-(phenylseleno)-naphthoquinones **13a–e** in high yield. Selenenylation of 2-bromo-3-(ethylthio)-1,4-naphthoquinone[2] **12f** also afforded the corresponding monoselenenylated naphthoquinone, compound **13f**, in 91% yield, but did not give the diselenenylated naphthoquinone **3** which would have been formed had the attack of phenyl selenide ion occurred on the carbon attached to the ethylthio group. This result is in accord with the fact that 2-(phenylseleno)naphthoquinone **2** did not act as a substrate for 2,3-bis(phenylseleno)naphthoquinone **3** (see the Scheme 2). In addition, the non-substituted naphthoquinone as well as 2-methyl- and 2-(ethylthio)naphthoquinone were inert to the present selenenylation. On the other hand, selenenylation of 2,3-dichloronaphthoquinone **12h** gave diselenonaphthoquinone **3** in high yield when selenenylated with phenyl selenide ion generated from diphenyl diselenide (1.1 mol equiv.), tributylphosphine (1.2 mol equiv.), and of NaOH (2.2 mol equiv.) [eqn. (2)].

It should be noted that selenenylation of 6- and 7-chloroquinolinequinone[17] **14a** and **14b** gave a 47% yield of 6-(phenylseleno)quinolinequinone **15a** and a 38% yield of 7-(phenylseleno)quinolinequinone **15b**, respectively, apparently *via ipso* attack of phenyl selenide ion [eqns. (3) and (4)].

Conclusions.—Various selenonaphthoquinones and quinolinequinones were synthesized from the halogenoquinones in high yield by a new method for the generation of phenyl selenide ion. Phenyl selenide ion was efficiently generated from diphenyl



Reagents and conditions: Bu_3P, aq. NaOH, THF, room temp.

diselenide by the action of tributylphosphine and aq. alkali. Phenyl selenide ion is believed to be generated from a selenophosphonium ion which liberates another phenyl selenide ion together with phosphine oxide. Phenyl selenide ion attacks carbons C-2 and C-3 2-bromo-1,4-naphthoquinone **1**, the former reaction being predominant to give 2-(phenylseleno)naphthoquinone **2**. Attack at the 3-position gives rise to monoselenonaphthoquinone **2** and 2,3-bis(phenylseleno)-naphthoquinone **3**. The formation of compound **3** was minimized in the reaction performed under oxygen-free conditions.

The present method provides a new, efficient generation of phenyl selenide ion. Further extensions and applications are currently under study.

Experimental

M.p.s were recorded on a Yanaco micro-melting point apparatus and are uncorrected. IR spectra were measured on KBr discs and/or film on a JASCO A-102 spectrometer. NMR spectra were determined using a JEOL JNM-PMX 60SI NMR spectrometer for solutions in deuteriochloroform with $SiMe_4$ as internal standard. Mass spectra were obtained with a Hitachi M-2000 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of Kyoto University. THF was distilled from sodium benzophenone ketyl under N_2 prior to use.

Physical, ^1H NMR, IR and MS spectroscopic data of all new selenonaphthoquinoes are summarized in Table 3. Satisfactory analytical data have been obtained on all these compounds.

Typical Procedure for Selenenylation. Preparation of 2-(*Phenylseleno*)-1,4-*naphthoquinone* **2**.—A solution of diphenyl diselenide (34 mg, 0.11 mmol) and tributylphosphine (24 mg, 0.12 mmol) in THF (0.5 cm^3) was vigorously agitated (vibrationally or ultrasonically) under argon for 5 min. To this mixture was added 10% aq. NaOH (88 mg, 0.22 mmol). The mixture was stirred for 15 min, during which time the two-phase mixture became homogeneous and the yellow solution turned colourless. The mixture was then added dropwise to a solution of 2-bromo-1,4-naphthoquinone **1** (47 mg, 0.20 mmol) in THF (0.5 cm^3) under argon and the mixture was stirred for a further 10 min. The mixture was poured into a mixture of brine (10 cm^3) and methylene dichloride (10 cm^3), and the aq. layer was extracted with methylene dichloride (2 × 5 cm^3). The combined extracts were washed with brine (5 cm^3), dried over $MgSO_4$, and evaporated. Column chromatography on silica gel with hexane–ethyl acetate (98:2) as eluent yielded 2-(phenylseleno)-1,4-naphthoquinone **2** (46 mg, 73%) and 2,3-bis(phenylseleno)-1,4-naphthoquinone **3** (11 mg, 11%).

Selenenylation of Compound **1** *under Completely Oxygen-free Conditions.*—The colourless mixture containing the phenylselenide ion obtained as above was cooled at −78 °C under argon and then evacuated (vacuum pump). The stopcock attached to the top of the flask was closed and then the mixture was gradually warmed up to room temperature, when argon gas was again introduced. These operations were repeated four or five times. The mixture thus obtained was added dropwise to a solution of 2-bromo-1,4-naphthoquinone **1** (47 mg, 0.2 mmol) in degassed THF (0.5 cm^3) at room temperature under argon. The mixture was stirred for 10 min. The work-up and purification described above gave 2-(phenylseleno)-1,4-naphthoquinone **2** (53 mg, 84%).

Selenenylation of 2,3-*Dichloro*-1,4-*naphthoquinone* **12h**.—The selenenylation of compound **12h** was carried out using diphenyl diselenide (1.10 mol equiv.), tributylphosphine (1.2 mol equiv.), aq. NaOH (2.20 mol equiv.). 2,3-Bis(phenylseleno)-1,4-naphthoquinone **3** (78 mg, 83%) was obtained.

Selenenylation of 2-*Bromo*-3-(*phenylseleno*)-1,4-*naphthoquinone* **11**.—The mixture containing sodium phenyl selenide as described in the typical procedure was added dropwise to a solution of 2-bromo-3-(phenylseleno)-1,4-naphthoquinone **11** (78 mg, 0.20 mmol) in THF (0.5 cm^3) under argon and was stirred for 10 min. The usual work-up and purification gave 2,3-bis(phenylseleno)-1,4-naphthoquinone **3** (83 mg, 89%).

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