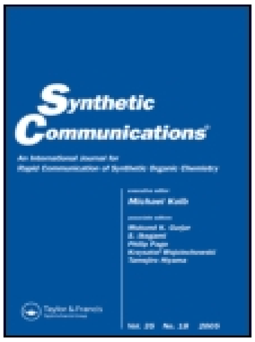

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SOME NOVEL QUINONE-TYPE COMPOUNDS CONTAINING ARYLSELENO GROUPS DERIVED FROM TETRACHLORO-1,4-BENZOQUINONE AND 2,3-DICHLORO-1,4-NAPHTHOQUINONE

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Abstract *Tetrachloro-1,2-benzoquinone and 2,3-dichloro-1,4-naphthoquinone react with a series of aryl and alkyl selenolate, generated either by the reaction of Grignard reagents and selenium powder or by the reduction of diselenides with* $NaBH_4$*, to give 3,6-diarylseleno-2,5-dichloro-1,4-benzoquinones 3 and 2,3-diarylseleno-1,4-naphthoquinones 4 in good yields.*

The chemistry of quinones is of interest both in natural product chemistry and in industrial chemistry.[1,2] A large variety of quinones have been used as synthetic intermediates, particularly in dye chemistry.[3] Recently, quinone-type dyestuffs have received increasing attention because of the search for new infrared dyes for optical recording media.[4]

2,3-Dichloro-1,4-naphthoquinone and tetrachloro-1,4-benzoquinone are versatile compounds with exceptionally reactive chlorine atoms and their chemistry is of theoretical and synthetic interest. They have been widely used as reagents, particularly in nucleophilic substitution. Numerous substituted quinones have been prepared previously by reactions of 2,3-dichloro-1,4-naphthoquinone or tetrachloro-1,4-benzoquinone with a variety of nucleophiles, such as alcohols and phenols,[5] thiols and thiophenols,[6] amines[7] and nitrogen containing heterocycles,[8] and phosphines.[9]

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Alkaneselenols and aromatic selenols are good nucleophiles, they react with alkyl halides, epoxides and diazo compounds to give the corresponding symmetrical or unsymmetrical selenides.[10] We have recently demonstrated that tetrachloro-1,4-benzoquinone **1** and 2,3-dichloro-1,4-naphthoquinone **2** react with a variety of alkyl telluroates to give 3,6-dialkyltelluro-2,5-dichloro-1,4-benzoquinones and 2,3-dialkyltelluro-1,4-naphthoquinones.[11] We now report the analogous reactions of chloroquinones **1** and **2** with selenolates.

Alkaneselenolates and aromatic selenolates are generally prepared by the reaction of Grignard reagents with controlled quantities of elemental selenium.[12] Thus, Grignard reagents from aryl halides reacted with selenium powder to give aryl selenolates, which were treated *in situ* with tetrachloro-1,4-benzoquinone **1** in THF under nitrogen to afford 3,6-diarylseleno-2,5-dichloro-1,4-benzoquinones **3a** to **3c** in 55 - 70% yield. Similar treatment of the phenyl and benzyl selenolate with 2,3-dichloro-1,4-naphthoquinone **2** gave 2,3-diarylseleno-1,4-naphthoquinones **4a** and **4b**, respectively (Method A).

Another clean and convenient generation of selenolates is the reduction of alkyl or aryl diselenides.[13] Various classes of selenides are synthesized by this method. Aryl selenolates, generated from the reductions of the corresponding diaryl diselenides **5a** and **5b**, reacted smoothly with 2,3-dichloro-1,4-naphthoquinone **2** in ethanol to form 2,3-diarylseleno derivatives **4a** and **4c** in good yields (Method B) as shown in Scheme and Table 1.

The products **3** and **4** were readily characterized by their elemental analyses and by their ^{1}H and ^{13}C NMR spectra. The structures of 3,6-disubstituted 1,4-benzoquinones were established by the spectra and the previously reported works.[5-8] In some cases, the carbonyl signal is too weak to be seen in the ^{13}C NMR spectra. In the IR spectra, the expected characteristic bands were found at 1655 - 1690 cm^{-1} for $\nu_{C=O}$. The visible absorption spectra were recorded in ethanol, the maximum absorption peak appeared around 450 nm with small extinction coeficients.

Scheme

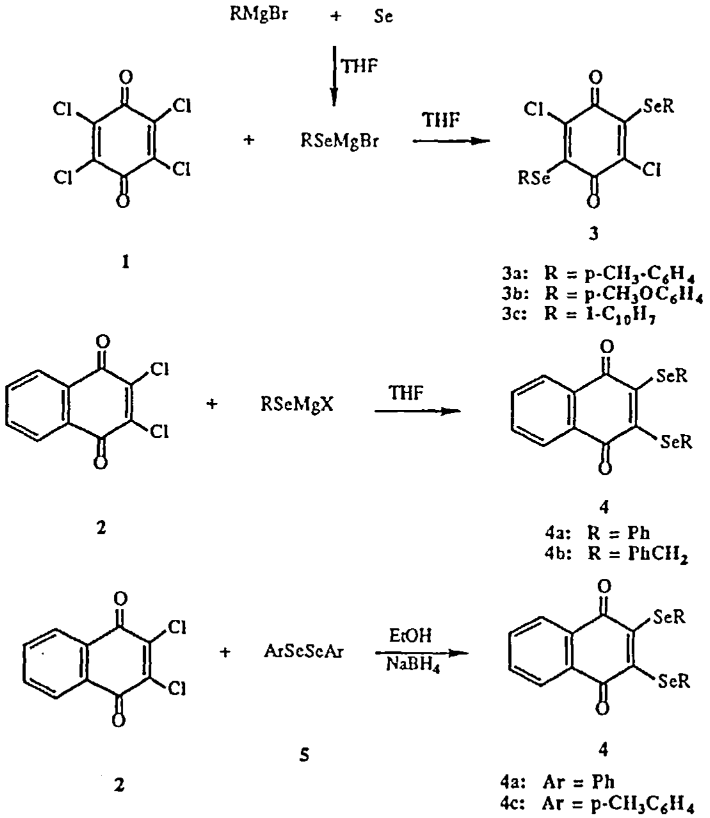

Table 1. Preparation of Arylseleno Derivatives 3 and 4

No.	Method	Yield(%)	mp (°C)	formula	Calcd. C	Calcd. H	Found C	Found H
3a	A	70	197-200	$C_{20}H_{14}Cl_2O_2Se_2$	46.63	2.74	46.90	2.69
3b	A	55	180-182	$C_{20}H_{14}Cl_2O_4Se_2$	43.90	2.58	44.19	2.56
3c	A	72	82-94	$C_{26}H_{14}Cl_2O_2Se_2$	53.18	2.40	53.00	2.18
4a	A	59	48-49	$C_{22}H_{14}O_2Se_2$	56.43	3.01	56.23	2.75
4a	B	70	48-49	$C_{22}H_{14}O_2Se_2$	56.43	3.01	56.11	3.14
4b	A	72	132-134	$C_{24}H_{18}O_2Se_2$	58.08	3.66	57.89	3.43
4c	B	64	168-170	$C_{24}H_{18}O_2Se_2$	58.08	3.66	57.63	3.30

Experimental

Melting points were measured on an electrothermal melting point apparatus and uncorrected. ^1H NMR spectra were obtained with a Varian VXR-300 (300 MHz, FT mode) or a JEOL JNM-PMX 60 SI (60 MHz) using TMS as internal standard. ^{13}C NMR spectra were recorded with a JOEL FX 100 (25.0 MHz) or a Varian VXR-300 (75.0 MHz) referenced on the solvent ($CDCl_3$ = 77.0 ppm and DMSO-d_6 = 39.5 ppm). IR spectra (KBr) were obtained on an IR-408 instrument. UV-visible spectra were determined on a UV-265 photospectroment. Elemental analyses were performed on a Carlo-Erba 1106 elemental analyser.

Tetrachloro-1,4-benzoquinone (Shanghai 1st Reagent Factory) and 2,3-dichloro-1,4-naphthoquinone (Aldrich), diphenyl diselenide (Fluka) were used without further purification. Tetrahydrofuran was dried by refluxing with benzophenone and sodium and used directly after distillation under dry nitrogen.

Preparation of arylseleno compounds via Grignard reaction, Method A:

A Grignard reagent prepared from magnesium turnings (0.48 g, 20 mmol) and an aryl halide (20 mmol) in THF (20 ml) was added to selenium powder under nitrogen. After the selenium powder had completely disappeared, tetrachloro-1,4-benzoquinone **1** or dichloro-1,4-naphthoquinone **2** (5 mmol in 10 ml of THF) was added dropwise to the solution. The mixture was stirred at room temperature for 4 hr, then poured into hydrochloric acid (2M), extracted with diethyl ether, washed with water and dried over $MgSO_4$. Removal of the solvent gave the crude product which was recrystallized from EtOH.

2,5-Dichloro-3,6-di-(4-methylphenylseleno)-1,4-benzoquinone (3a)

δ_H: 7.50 (4H, d), 7.06 (4H, d), 2.00 (6H, s, 2xCH_3); δ_C: 148.9, 143.9, 137.5, 131.6, 129.8, 120.6, 20.6 (CH_3); ν(KBr): 1690, 1570, 1460, 910, 750, 710 cm^{-1}; λ_{max}: 460.4 nm (ε = 1300).

2,5-Dichloro-3,6-di-(4-methoxyphenylseleno)-1,4-benzoquinone (3b)

δ_H: 7.70 (4H, d), 5.83 (4H, d), 3.80 (6H, s, 2xOCH_3); δ_C: 177.0, 151.1, 135.3, 134.6, 134.4, 127.2, 120.9, 115.0, 55.2 (OCH_3); ν(KBr): 1685, 1590, 1490, 1170, 820 cm^{-1}; λ_{max}: 452.0 nm (ε = 2040).

2,5-Dichloro-3,6-di-(1-naphthylseleno)-1,4-benzoquinone (3c)

δ_H: 8.30 (2H, d), 8.17 (2H, d), 7.83 (2H, d), 7.70 (2H, d), 7.46 (2H, d), 7.40 (2H, d), 7.20 (2H, d); δ_C: 176.0, 133.6, 133.3, 133.0, 129.8, 128.9, 128.6, 127.1, 126.9, 126.5, 125.8; ν(KBr): 3050, 1680, 1590, 1500, 790, 770 cm^{-1}; λ_{max}: 440.0 nm (ε = 1600).

2,3-Di-(phenylseleno)-1,4-naphthoquinone (4a)

δ_H: 7.75-7.70 (m, 2H), 7.65 (4H, m), 7.50 (2H, d), 7.20 (6H, m); δ_C: 175.6, 142.0, 133.5, 133.0, 129.9, 129.6, 128.5, 127.1, 126.3; ν(KBr): 3010, 1655, 1590, 1200, 740, 690 cm^{-1}; λ_{max}: 436.4 nm (ε = 3240).

2,3-Di-(benzylseleno)-1,4-naphthoquinone (4b)

δ_H: 7.80-7.57 (4H, m), 7.40-7.20 (10H, m), 3.57 (4H, s, CH_2); δ_C: 141.8, 138.1, 133.6, 127.8, 127.4, 126.5, 125.6, 125.1, 121.3, 26.5 (CH_2); ν(KBr): 3050, 1670, 1450, 760, 700 cm^{-1}; λ_{max}: 470.6 nm (ε = 3310).

Preparation of aryseleno derivatives via reduction of diselenides, Method B

Diphenyl diselenide (2 g, 5 mmol) dissolved in absolute ethanol was stirred with $NaBH_4$ (10 mmol) at room temperature for 2 hrs. 2,3-Dichloro-1,4-naphthoquinone (5 mmol) was added and the mixture was stirred overnight. The reaction was quenched with dilute hydrochloric acid (2 M), and the product was extracted with chloroform, washed with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to obtain the product, which was crystallized from ethanol.

2,3-Di-(4-methylphenylseleno)-1,4-naphthoquinone (4c)

δ_H: 7.84-7.60 (4H, m), 7.32 (4H, d), 7.01 (4H, d), 2.32 (6H, s, CH_3); δ_C: 175.8, 142.7, 134.8, 132.8, 130.0, 129.5, 128.8, 128.0, 122.1, 21.0 (CH_3); ν(KBr): 1660, 1500, 1270, 1140, 710 cm^{-1}.

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