PREPARATION AND INTERCONVERSION OF PHENYLSELENENYLATED AND ALKYLSELENENYLATED AROMATIC COMPOUNDS

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Abstract - Phenylselenenyl and alkylselenenyl sulfates were found to efficiently and mildly introduce one or several phenylselenenyl or alkylselenenyl groups into activated aromatic or heteroaromatic compounds. When treated with methylselenenyl sulfate, veratrole and 2,2',3,3'-tetramethoxybiphenyl afforded 2,3,7,8-tetramethoxyselenanthrene and 2,3,7,8-tetramethoxydibenzoselenophene, respectively, *via* oxidative demethylation at selenium/cyclization. Phenylselenenylated thiophenes were selectively hydrodeselenenated at the 2- and/or 5-positions by treatment with the appropriate amount of n-butyllithium at -78° C followed by hydrolysis.

INTRODUCTION

Due to the rich and diverse chemistry of selenium, many methods are now available for the selenenylation of aromatic compounds.[1,2] Highly nucleophilic areneselenolate ions undergo aromatic nucleophilic substitution when treated with aryldiazonium salts or electron deficient aryl halides. The photo- and copper-promoted reactions of benzeneselenolate ion with unactivated haloarenes are also successful for

diaryl selenide synthesis. Aromatic Grignard reagents and aryllithiums attack diaryl diselenides and arylselenocyanates on selenium to provide diaryl selenides. Aromatic electrophilic substitution using benzeneselenenyl chloride[3] or cyanide, phenylselenenyl hexafluorophosphate[4] and (phenylselenenyl)-dimethylsulfonium tetrafluoroborate[5] was used for the low-yield phenylselenenylation of various activated aromatic compounds. Recently, several attempts were made to produce electrophilic organoselenium reagents by electrochemical,[6] photochemical[7] or chemical oxidation[8-10] of diphenyl diselenide.

We have studied for some time the reactions of phenylselenenyl sulfate (**1**)[11] and alkylselenenyl sulfates (**2**) with aromatic and heteroaromatic compounds. A recent paper by Tiecco and co-workers,[12] concerning the reactions of reagent (**1**) with thiophenes has prompted us to disclose our findings in this area.

$PhSeOSO_3^- NH_4^+$ $RSeOSO_3^- NH_4^+$

1 **2a** R = methyl
b R = 1-butyl
c R = 1-oktyl

RESULTS AND DISCUSSION

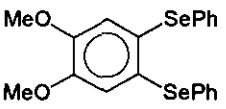
Benzeneselenenyl sulfate was prepared as previously described[11] in methanol and heated at reflux with a series of aromatic compounds. As shown in Table 1, monoselenenylated compounds were usually isolated in fair to good yields from activated aromatics according to eq. 1. In contrast, benzene and toluene did not give a substitution product when heated for a long time with phenylselenenyl sulfate. Veratrole afforded a bisphenylselenenylated product (**3**) as a major product when stoichiometric amounts of the reactants were used. When the phenylselenenylating agent was used in excess, compound (**3**) was isolated in 75% yield.

$$(1) \quad Ar-H + PhSeOSO_3^- NH_4^+ \xrightarrow{MeOH} ArSePh + HSO_4^- + NH_4^+$$

Table 1 Phenylselenenylation of Aromatic Compounds

Aromatic Compound	Reaction time (h)	Ar in equation 1	Yield (%)	mp (°C)	Lit. mp[ref] (°C)
anisole	24	4-methoxyphenyl	79	42-43	46.3[24]
phenol	3	4-hydroxyphenyl	65	52-53	52-53[5]
N,N-dimethylaniline	24	4-(*N,N*-dimethylamino)phenyl	37	67	67-68[5]
benzene	16	phenyl	0		
toluene	16	4-methylphenyl	0		

When dimethyl diselenide was heated in refluxing methanol for 1 h with a slight excess of ammonium peroxydisulfate, methylselenenyl sulfate (**2a**) was generated. However, addition of anisole, *N,N*-dimethylaniline or veratrole, respectively, and continued heating at reflux afforded the corresponding methylselenenylated compounds (**4a**) (12%), (**4b**) (18%) and (**5**) (27%) only in low isolated yields.



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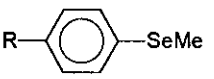
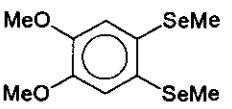


4 a R = OMe
b R = NMe_2



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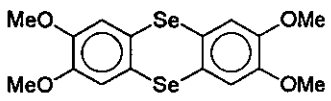
Interestingly, in the preparation of compound (**5**), tetramethoxyselenanthrene (**6**) (30%) was also isolated. This product is probably formed via persulfate induced oxidation/demethylation of the two methylselenenyl groups and reaction of the resulting bis-electrophile with veratrole. When 3,3',4,4'-tetramethoxybiphenyl was treated with a five-fold excess of the methylselenenylating agent (**2a**), dibenzoselenophene (**7**) was isolated in almost quantitative yield. A similar but less efficient conversion was observed when the biphenyl was treated with reagents (**2b**) and (**2c**) (87% and 50% yields, respectively, of the dibenzoselenophene were isolated). Clearly, all these transformations have to involve oxidative dealkylation at selenium and electrophilic ring-closure.



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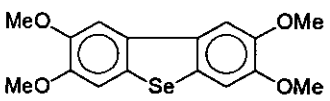

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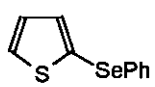
As discovered independently by Tiecco[12] and us, thiophene is highly reactive towards electrophilic selenenylating agents. Furthermore, the firstly introduced organylselenenyl group activates the thiophene nucleus substantially to further electrophilic attack. Upon addition of a 40-fold excess of the heterocycle to a solution of reagent (**1**) at ambient temperature, we were able to isolate compound (**8**) in 53% yield. Prolonged heating of thiophene with an excess of phenylselenenyl sulfate resulted in the formation of readily separable mixtures of bis-, tris- and tetrakisphenylselenenylated products (**9**, **10** and **11a**).[12]



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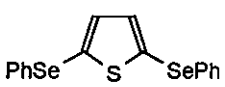

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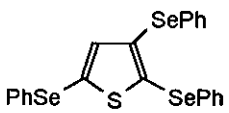

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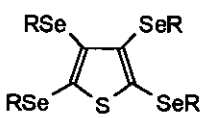
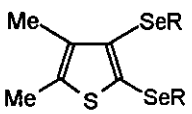
In our hands the best yield of compound (**11a**) (87%) was obtained by heating of compound (**9**) with a 3.5-fold excess of reagent (**1**) under N_2 for 6 days.



11 a R = phenyl
b R = methyl
c R = 1-butyl
d R = 1-octyl



12 a R = methyl
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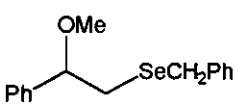

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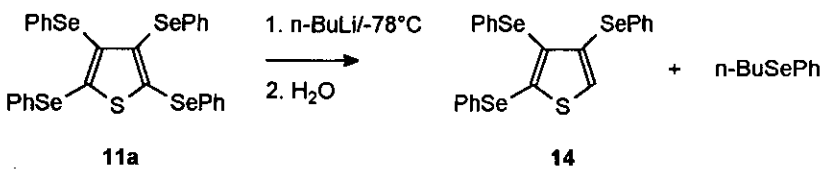
The sterically less demanding methylselenenyl group is more readily introduced into thiophene than the phenylselenenyl group. Thus, treatment of thiophene with a 4.6-fold excess of methylselenenyl sulfate (**2a**) for 24 h in refluxing methanol afforded compound (**11b**) as the only product (74% yield). Similarly, 1-butylselenenyl sulfate (**2b**) and 1-octylselenenyl sulfate (**2c**) afforded the corresponding tetrakis-alkylselenenylated thiophenes (**11c**) and (**11d**) in 77% and 14% yields, respectively. In the latter reaction,

the 2,3,5-trisalkylselenenylated (49%) and the 2,5-bisalkylselenenylated (5%) compounds were also isolated. 2,3-Dimethylthiophene was readily bisalkylselenenylated by all three reagents (**2**) to afford compounds (**12a**) (75%) (**12b**) (73%) and (**12c**) (91%), respectively.

Attempts to similarly introduce benzylselenenyl groups into thiophenes and other activated aromatics met with failure. On the other hand, styrene afforded a methoxyselenenylation product (**13**) in fair yield (52%) under the ordinary reaction conditions. This seems to indicate that formation of the selenenylating reagent from dibenzyl diselenide is not the problem. All attempts to generate *t*-butylselenenyl sulfate met with failure.

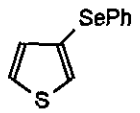
It is known that α-halogens of thiophenes are selectively removed by treatment with zinc. In an attempt to similarly obtain a 2,5-unsubstituted phenylselenenylated thiophene, suitable for polymerisation, compound (**11a**) was heated with an excess of zinc in acetic acid. However, only a slow conversion to trisphenylselenenylated thiophene (**14**) was observed. Instead, lithium-selenium exchange[13] turned out to be very efficient to bring about hydrodeselenenation at positions 2 and 5 of phenylselenenylated thiophenes prepared. Thus, treatment of compound (**11a**) with one equivalent of butyllithium in THF at -78°C, followed by hydrolytic work-up, afforded compound (**14**) in 65% yield in addition to butyl phenyl selenide (eq. 2).

(2)



11a **14**

Similarly, compounds (**15**) (100%) and (**16**) (78%) were obtained from compounds (**10**) and (**11a**), respectively, on treatment with two equivalents of butyllithium. Attempts to similarly remove alkylselenenyl groups from compounds (**11b**) and (**11c**) resulted in the formation of complex product mixtures. This may be due to the presence of acidic protons α to selenium.



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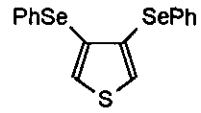

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CONCLUSIONS

We have demonstrated that not only phenylselenenyl groups but also a variety of alkylselenenyl groups can be readily introduced into various activated aromatic compounds. In some cases, the alkylselenenyl group undergoes oxidative dealkylation and further electrophilic attack resulting in a net introduction of a Se^{2+} electrophile into the aromatic compound. In view of the ready reductive dealkylation of alkylselenenylated aromatics,[14] we feel that the methodology presented in this paper would be of considerable interest for the preparation of selenium-rich donors for ion radical salts.[15] The hydrodeselenation reactions described, resulting in the formation of phenylselenenylated 2,5-unsubstituted thiophenes, would hopefully find use for the preparation of selenium-rich polythiophenes.[16]

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H Nmr spectra were recorded in $CDCl_3$ at 300 MHz using tetramethylsilane as an internal standard. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany. Dimethyl diselenide (98%) and diphenyl diselenide (98%) are commercially available. Di-n-butyl and di-n-octyl diselenide were prepared from disodium diselenide[17] and the corresponding alkyl bromides and dibenzyl diselenide from dilithium diselenide[18] and benzyl bromide in analogy with literature procedures. 3,3',4,4'-Tetramethoxybiphenyl[19] and 2,3-dimethylthiophene[20] were prepared according to published methods.

Electrophilic Aromatic Selenenylation. Typical procedure.

2,3,4,5-Tetrakis(methylselenenyl)thiophene (11b). Dimethyl diselenide (0.42 g, 2.19 mmol) and ammonium peroxydisulfate (0.61 g 98%, 2.62 mmol) were heated at reflux for 1 h in methanol (5 ml). After addition of thiophene (0.08 g, 0.95 mmol) and heating at reflux for 24 h, the reaction mixture was

allowed to cool. Treatment with water/methylene chloride, separation of the organic phase, drying ($CaCl_2$), evaporation and flash chromatography (SiO_2, pentane) followed by recrystallization from pentane afforded the title compound (0.32 g, 74%), mp 45-46°C. Anal. Calcd for $C_8H_{12}SSe_4$: C, 21.07; H, 2.65. Found: C, 20.89; H, 2.64. ^{1}H Nmr ($CDCl_3$): δ 2.41 (s, 6H), 2.30 (s, 6H).

The following compounds were similarly prepared. Reagents (**1**, **2b** and **2c**) were prepared from the corresponding diselenides and ammonium peroxydisulfate in an analogous manner. The appropriate aromatic compound was then heated at reflux with the selenenylating reagent for *a* hours. The molar ratio, selenenylating agent/aromatic compound = *b*/*c* is also given.

4-Methoxyphenyl phenyl selenide. *b*/*c* = 5/1. For *a*, yield, mp and lit. mp, see Table 1.

4-Hydroxyphenyl phenyl selenide. *b*/*c* = 1.1/1. For *a*, yield, mp and lit. mp, see Table 1.

4-(*N*,*N*-Dimethylamino)phenyl phenyl selenide. *b*/*c* = 2/1. For *a*, yield, mp and lit. mp, see Table 1.

4,5-Bis(phenylselenenyl)veratrole (3). Oil; *a* = 24; *b*/*c* = 2.7/1. Yield 75%. Anal. Calcd for $C_{20}H_{18}O_2Se_2$: C, 53.59; H, 4.05. Found: C, 53.53; H, 3.97. ^{1}H Nmr δ 7.45-7.48 (several peaks, 4H), 7.26-7.31 (several peaks, 6H), 6.81 (s, 2H), 3.68 (s, 6H).

Methyl 4-methoxyphenyl selenide (4a). Oil; *a* = 24; *b*/*c* = 2/1. Yield 12%. The compound was identical to an authentic sample of the material.[21]

Methyl 4-(*N*,*N*-dimethylamino)phenyl selenide (4b). Oil; *a* = 24; *b*/*c* = 2/1. Yield 18%. The compound was identical to an authentic sample of the material.[21]

4,5-Bis(methylselenenyl)veratrole (5). Oil; *a* = 24; *b*/*c* = 2/1. Yield 27%. Anal. Calcd for $C_{10}H_{14}O_2Se_2$: C, 37.06; H, 4.35. Found: C, 37.22; H, 4.32. ^{1}H Nmr δ 6.93 (s, 2H), 3.87 (s, 6H), 2.32 (s, 6H). Under these conditions compound (**6**) was also isolated in 30% yield (*vide infra*).

2,3,7,8-Tetramethoxydibenzoselenophene (7). *a* = 24; *b*/*c* = 5/1. Yield 99%. The compound was identical to an authentic sample of the material.[22]

2,5-Bis(phenylselenenyl)thiophene (9). *a* = 2; *b*/*c* = 1/1. Yield 79%, mp 46-47°C (lit., mp 47-48 °C).[12]

2,3,5-Tris(phenylselenenyl)thiophene (10). *a* = 24; *b/c* = 4/1. Yield 85%, mp 76-77°C (lit., mp 77-78 °C).[12]

2,3,4,5-Tetrakis(phenylselenenyl)thiophene (11a) was prepared starting from compound (**9**). The reaction was run under an atmosphere of dry nitrogen. *a* = 6 days; *b/c* = 3.5. Yield 87%. mp 112.5-113.5 °C (lit., mp 105-108 °C).[12]

2,3,4,5-Tetrakis(1-butylselenenyl)thiophene (11c). Oil; *a* = 24; *b/c* = 5/1. Yield 77%. Anal. Calcd for $C_{20}H_{36}SSe_4$: C, 38.47; H, 5.81 . Found: C, 38.60; H, 5.85. ^{1}H Nmr δ 2.96 (t; J = 7.4 Hz, 4H), 2.90 (t; J = 7.4 Hz, 4H), 1.67-1.75 (several peaks, 4H), 1.54-1.64 (several peaks, 4H), 1.36-1.50 (several peaks, 8H), 0.92 (t; J = 7.4 Hz, 6H), 0.88 (t; J = 7.4 Hz, 6H).

2,3,4,5-Tetrakis(1-octylselenenyl)thiophene (11d). Oil; *a* = 24; *b/c* = 5/1. Yield 14%. Anal. Calcd for $C_{36}H_{68}SSe_4$: C, 50.90; H, 8.10. Found: C, 51.08; H, 7.95. ^{1}H Nmr δ 2.94 (t; J = 7.2 Hz, 4H), 2.89 (t; J = 7.5 Hz, 4H), 1.71-1.76 (several peaks, 4H), 1.58-1.63 (several peaks, 4H), 1.21-1.43 (several peaks, 40H), 0.87 (t; J = 6.3 Hz, 12H).

2,3,5-Tris(1-octylselenenyl)thiophene was also isolated as an oil in the preparation of compound (**11d**). Yield 49%. Anal. Calcd for $C_{28}H_{52}SSe_3$: C, 51.14; H, 7.97. Found: C, 50.86; H, 7.84. ^{1}H Nmr δ 7.03 (s, 1H), 2.88 (t; J = 7.4 Hz, 2H), 2.86 (t; J = 7.4 Hz, 2H), 2.81 (t; J = 7.4 Hz, 2H), 1.68-1.70 (several peaks, 6H), 1.26-1.39 (several peaks, 30H), 0.88 (t; J = 6.5 Hz, 9H).

4,5-Dimethyl-2,3-(methylselenenyl)thiophene (12a). Oil; *a* = 3; *b/c* = 2/1. Yield 75%. Anal. Calcd for $C_8H_{12}SSe_2$: C, 32.23; H, 4.06. Found: C, 32.34; H, 3.93. ^{1}H Nmr δ 2.36 (s, 3H), 2.35 (s, 3H), 2.23 (s, 3H), 2.15 (s, 3H).

4,5-Dimethyl-2,3-bis(1-butylselenenyl)thiophene (12b).Oil; *a* = 2; *b/c* = 3/1. Yield 73%. Anal. Calcd for $C_{14}H_{24}SSe_2$: C, 43.98; H, 6.33. Found: C, 43.88; H, 6.21. ^{1}H Nmr δ 2.88 (t; J = 7.2 Hz, 2H), 2.71 (t; J = 7.2 Hz, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 1.67-1.72 (several peaks, 2H), 1.54-1.59 (several peaks, 2H), 1.38-1.46 (several peaks, 4H), 0.91 (t; J = 7.5 Hz, 3H), 0.88 (t; J = 7.2 Hz, 3H).

4,5-Dimethyl-2,3-bis(1-octylselenenyl)thiophene (12c). Oil; *a* = 24; *b/c* = 3/1. Yield 91%. Anal. Calcd for $C_{22}H_{40}SSe_2$: C, 53.43; H, 8.15. Found: C, 53.50; H, 8.07. ^{1}H Nmr δ 2.87 (t; J = 7.5 Hz, 2H), 2.70 (t; J = 7.5 Hz, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 1.66-1.75 (several peaks, 2H), 1.53-1.63 (several peaks, 2H), 1.18-1.42 (several peaks, 20H), 0.87 (t; J = 6.3 Hz, 6H).

2,3,7,8-Tetramethoxyselenanthrene (6) was best prepared using a 50% excess of ammonium peroxydisulfate in the preparation of the methylselenenylating reagent. *a* = 24; *b/c* = 5/1. Yield 42%. The compound was identical to an authentic sample of the material.[23] Under these conditions compound (**5**) was also isolated in 11% yield (*vide supra*).

2-(Phenylselenenyl)thiophene (8). A solution of phenylselenenyl sulfate was prepared as described in the typical procedure from diphenyl diselenide (0.50 g, 1.57 mmol). To the cooled solution of the reagent was added thiophene (10.65 g, 0.13 mol). After stirring for 1 h, heating at reflux for 1 h and work up as described in the typical procedure, the title compound (**8**) (0.40 g, 53%) was isolated, by bulb-to-bulb distillation, as an oil. Trace amounts of diphenyl diselenide was removed from the product by $NaBH_4$-reduction in ethanol, dilution with water and extraction with diethyl ether. Anal. Calcd for $C_{10}H_8SSe$: C, 50.21; H, 3.37. Found: C, 50.36; H, 3.51. ^{1}H Nmr δ 7.47 (dd; J = 5.4 and 0.3 Hz, 1H), 7.31-7.35 (several peaks, 3H), 7.19-7.26 (several peaks, 3H), 7.05 (dd; J = 5.4 and 3.3 Hz, 1H).

Benzyl 2-methoxy-2-phenylethyl selenide (13).

Dibenzyl diselenide (0.60 g, 1.76 mmol) and ammonium peroxydisulfate (0.49 g, 2.12 mmol) were heated at reflux for 1.5 h in methanol (10 ml). After cooling, addition of styrene (0.36 g, 3.46 mmol) and stirring for 30 min, the reaction mixture was worked up as described in the typical procedure. The title compound (**13**) (0.55 g, 52%) was isolated as an oil. Anal. Calcd for $C_{16}H_{18}OSe$: C, 62.95; H, 5.94. Found: C, 62.85; H, 5.81. ^{1}H Nmr δ 7.19-7.35 (several peaks, 10H), 4.19 (m, 1H), 3.69 (s, 2H), 3.21 (s, 3H), 2.89 (dd; J = 12.8 and 8.1 Hz, 1H), 2.65 (dd; J = 12.8 and 5.4 Hz, 1H).

2,3,4-Tris(phenylselenenyl)thiophene (14)

To a stirred solution of compound **(11a)** (0.22 g, 0.31 mmol) in THF (5 ml) at -78 °C was added n-butyllithium (0.22 ml, 1.46 M, 0.32 mmol) by syringe. After 45 min at -78 °C the cooling bath was removed and water (1 ml) added. Workup as described in the typical procedure afforded the title compound **(14)** (0.11 g, 65%) as an oil. Anal. Calcd for $C_{22}H_{16}SSe_3$: C, 48.10; H, 2.94. Found: C, 47.98; H, 2.94. ^{1}H Nmr δ 7.47-7.51 (several peaks, 4H), 7.23-7.29 (several peaks, 8H), 7.13-7.17 (several peaks, 3H), 6.97 (s, 1H).

3-(Phenylselenenyl)thiophene (15). By using the procedure for the preparation of compound **(14)**, compound **(10)** was treated with 2.0 equivalents of n-butyllithium to afford the title compound as an oil in 100 % yield. Anal. Calcd for $C_{10}H_8SSe$: C, 50.01; H, 3.36. Found: C, 49.97; H, 3.41. ^{1}H Nmr 7.48 (d; J = 1.5 Hz, 1H), 7.35-7.40 (several peaks, 3H), 7.22-7.28 (several peaks, 4H).

3,4-Bis(phenylselenenyl)thiophene (16). By using the procedure for the preparation of compound **(14)**, compound **(11a)** was treated with 2.0 equivalents of n-butyllithium to afford the title compound as an oil in 78 % yield. Anal. Calcd for $C_{16}H_{12}SSe_2$: C, 48.74; H, 3.07. Found: C, 48.83; H, 3.16. ^{1}H Nmr δ 7.42-7.46 (several peaks, 4H), 7.26-7.29 (several peaks, 8H).

ACKNOWLEDGEMENT

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