

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Electrophilic Organoselenium Reagents; Approaches to the Synthon Phenylselenium ION (PhSe⁺).

Lars Henriksen; Nicolai Stuhr-Hansen

To cite this Article Henriksen, Lars and Stuhr-Hansen, Nicolai(1998) 'Electrophilic Organoselenium Reagents; Approaches to the Synthon Phenylselenium ION (PhSe⁺).', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 175 — 190

To link to this Article: DOI: 10.1080/10426509808545942

URL: <http://dx.doi.org/10.1080/10426509808545942>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

**ELECTROPHILIC ORGANOSELENIUM REAGENTS;
APPROACHES TO THE SYNTHON
PHENYLSELENIUM ION (PhSe⁺).**

LARS HENRIKSEN and NICOLAI STUHR-HANSEN
Department of Chemistry, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen, Denmark.

A mixture of benzeneseleninic acid (**1**) and diphenyl diselenide (**2**) gives *o*-specific phenylselenenylation of phenols by an ene-mechanism. The reagent couple dihydroxy phenyl selenonium *p*-toluenesulfonate (**14a**)-**2** phenylselenenylates a range of arenes with high *p*-selectivity by transfer of phenylselenenium ion. The reactivity of the latter reagent is enhanced with increasing acidity of the solvent. ⁷⁷Se NMR shows that both reagents in hydroxylic solvents contain essentially a mixture of **2** and a compound with the seleninic oxidation stage while the formation of phenylselenenium ion is observed in the presence of a perfluorinated co-solvent.

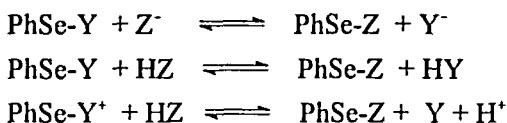
Keywords. Benzeneseleninic acid; diphenyl diselenide; dihydroxy phenyl selenonium ion; ⁷⁷Selenium NMR; (phenylselenenyl)arenes; (phenylseleno)benzoquinones.

INTRODUCTION

The introduction, in the middle 1970ties, of selenium containing control functions for various synthetic purposes aroused an interest in reactions which could attach a selenium atom to a specific position in a carbon skeleton. Arylseleno functions are frequently used in order to

ensure reaction to the desired side of the selenium atom. Among these the phenylseleno group is the most readily available and consequently the one most commonly used. One major route to phenylseleno-substituted compounds utilizes electrophilic Se-species which transfer the PhSe^+ synthon to a nucleophilic carbon site. The principal types of transfer reaction are shown in SCHEME 1, in which Y denotes any atom or atom group which may form a stable anion or may be protonated to give a stable species and Z represents the nucleophilic carbon site (*e.g.* a carbanion, an alkene, an enol or an arene). Note that the transfer reactions are in principle reversible. For example, enolate ions react with diphenyl diselenide to give α -phenylselenylated carbonyl compounds. The products on treatment with selenophenol reverts to the starting carbonyl compound and diphenyl diselenide. The development in this area has been reviewed up to 1985 (see *e.g.* refs.^{1,2}).

SCHEME 1. PhSe^+ - transfer reactions.



The actual reagents used for phenylselenium ion transfer cover a wide range of reactivities. Diphenyl diselenide ($\text{Y} = \text{SePh}$) and phenyl selenocyanate ($\text{Y} = \text{CN}$) are used mostly with carban-ions. The phenylselenenyl halides ($\text{Y} = \text{Cl}, \text{Br}$) and the related N-phenylselenophthalimide³ also react with neutral substrates, *e.g.* alkenes and enolizable carbonyl compounds. More recently a number of reagents listed in TABLE I have been shown to effect phenylselenium transfer to aromatic substrates. The present account gives some mechanistic and preparative conclusions derived from our studies of the two last reagent couples of TABLE I as well as the results of a ^{77}Se NMR

study of various phenylselenylation reagents.

TABLE 1. Reagents for phenylselenylation of arenes.

Reagent	Substrates ^a	Ref.
PhSeSMe ₂ ⁺ BF ₄ ⁻	A,B	4
PhSePF ₆	A,B,C	5
PhSeSePh/(NH ₄) ₂ S ₂ O ₈	B,D	6,7
PhSeSePh/m-NO ₂ C ₆ H ₄ SO ₂) ₂ O ₂	A,B,C,E	8
PhSeSePh/PhSeO ₂ H	A ^b	9
PhSeSePh/PhSeO ₂ H/TsOH	A,B	9

^a A: Phenols, B: Anisols; C: Alkylbenzenes; D: Thiophene; E: anilines and anilides. ^b Phenylselenylated by-products previously observed during oxidations of phenols with benzeneseleninic acid are probably produced by this reagent.

BENZENESELENINIC ACID - DIPHENYL DISELENIDE.

A mixture of benzeneseleninic acid (1) and diphenyl diselenide (2) may, regardless of its origin, serve as a phenylselenyl transfer reagent. It is assumed that benzeneselenenic acid (3) - or its anhydride (4) - formed in equilibrium with 1 and 2 (SCHEME 2) is the actual reagent although no such species has been observed. All observations on stable derivatives of selenenic acids refer to species with a non-bonded

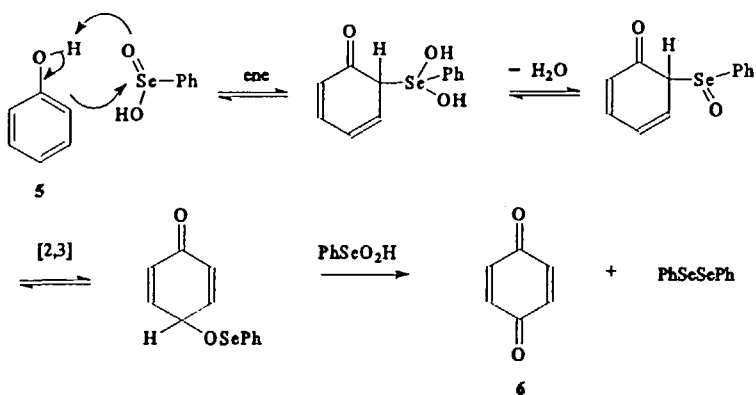
SCHEME 2.



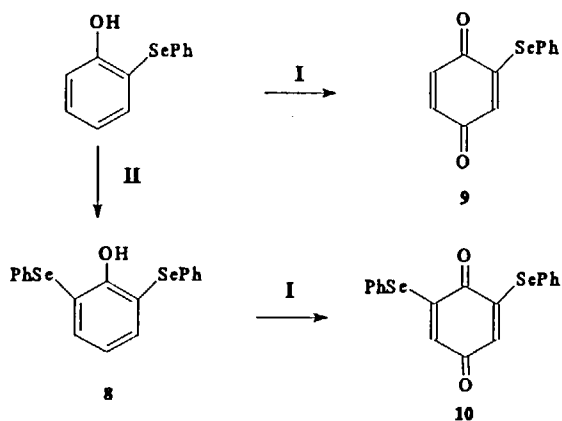
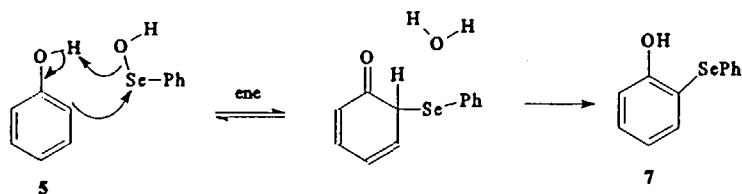
intramolecular stabilization, *e.g.* by a nitro- or benzoyl group.¹⁰

SCHEME 3.

I. Oxidation



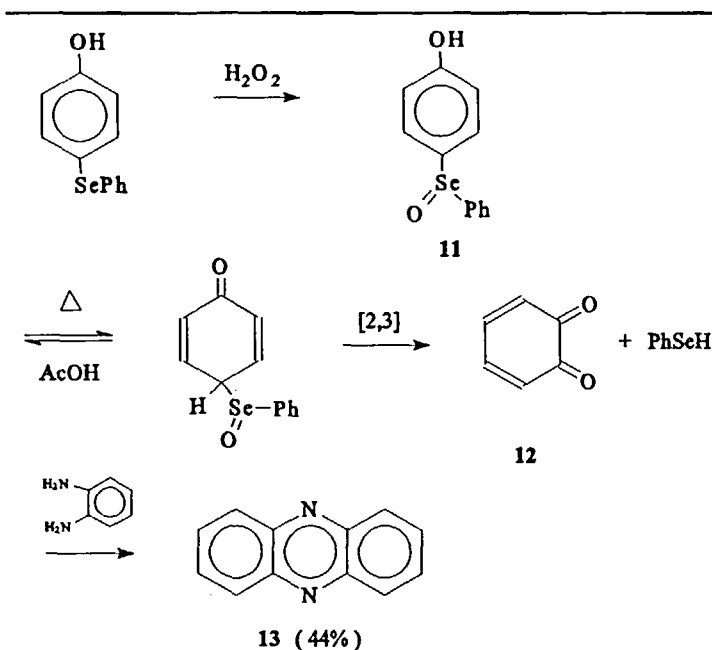
II. Phenylselenenylation



The Barton group has shown that the oxidation of phenols with benzeneseleninic anhydride gives *o*-quinones by a [2,3]-shift in an intermediary arylseleninate.¹¹ It was also noted that oxidation with **1** could give *p*-quinones by a different but not clarified path.¹²

We found⁹ that the reaction of phenol (**5**) with **1** gives 5 products: 1,4-benzoquinone (**6**), 2-(phenylseleno)phenol (**7**), 2,6-bis(phenyl-seleno)phenol (**8**), 2-phenylseleno-1,4-benzoquinone (**9**) and 2,6-bis(phenylseleno)-1,4-benzoquinone (**10**). Solvents acting as hydrogen bond acceptors strongly retard the over-all reaction without affecting the product distribution. Anisole is inert towards the reagent. We therefore concluded that both the oxidation and the specific *o*-phenylselenylation reaction are initiated by ene-reactions involving the phenolic hydrogen as shown in SCHEME 3.

SCHEME 4.

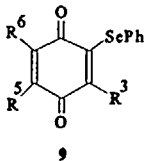
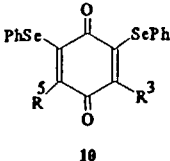


Further evidence for an initial *o*-attack in the formation of the *p*-quinones is found in the observation¹³ that *p*-hydroxyphenyl phenyl selenoxide (11), a tautomer of the intermediate for *p*-attack of 1 on phenol, on treatment with acetic acid in dichloromethane rearranged to *o*-benzoquinone (12), trapped with *o*-phenylenediamine as phenazine (13) while only traces of 6 was observed (SCHEME 4).

We have occasionally observed the formation of compounds 6-10 upon heating of samples of 1 prepared by hydrogen peroxide oxidation of 2. This result is explained by a contamination with benzeneperoxoseleninic acid which produces phenol by a Baeyer-Villiger rearrangement. It is reproduced by heating 1 with a few percent 35% hydrogen peroxide added or alternatively by refluxing 1 with ammonium peroxodisulfate in methanol.

The processes shown in SCHEME 3 are not ideal for prepara-

TABLE 2. Phenylseleno-substituted 1,4-benzoquinones.¹³

				<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>9</p> </div> <div style="text-align: center;">  <p>10</p> </div> </div>		
Type	R ³	R ⁵	R ⁶	Yield (%)	M.p. (°C)	Vis. absorption λ _{max} (nm), log ε
9	H	H	H	28	113-114	455 (3.42)
9	H	H	Me	21	99-101	446 (3.33)
9	H	Me	H	20	111-112	446 (3.30)
9	H	Me	Me	17	97-98	444 (3.27)
9	Me	Me	H	15	39-40	456 (3.17)
9	H	H	Ph	22	132-133	458 (3.38)
9	H	OMe	H	50	168-169	446 (2.48)
10	H	H		16	219-220	413 (3.69); 511 (3.50)
10	Me	Me		5	136-137	446 (3.31); 495 (sh)
10	H	Me		13	85-86	424 (3.35); 495 (sh)

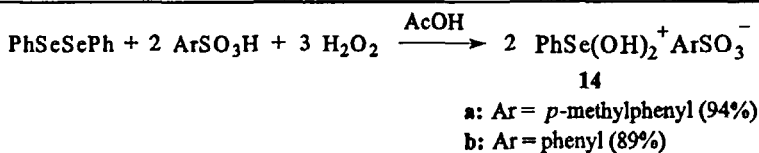
tive purposes. The reaction mixtures are complex and the yields of any particular product seldom exceeds 30%. However, the reaction which is general for 2,4-unsubstituted phenols do afford a route to the otherwise not easily accessible *o*-(phenylseleno)phenols, 7 and 8, and (phenylseleno)quinones, 9 and 10. In particular the latter compounds are interesting materials. They are dyes with red to violet colours, not degraded by ordinary daylight, resistant toward aqueous acid and base and thermally stable up to at least 150°C. A series of compounds 9 and 10 are presented in TABLE 2.

THE REAGENT COUPLE DIHYDROXY PHENYLSELENONIUM ION - DIPHENYL DISELENIDE.

The addition of one equivalent of a strong acid to the reagent system 1-2 has three conspicuous consequences:⁹ The rate of disappearance of 1 increases by more than a factor 20, anisole is also phenylselenylated and the reaction course changes from *o*-specificity to a high degree of *p*-selectivity.

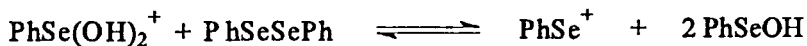
Compound 1 is sufficiently basic to give stable salts with strong acids with non-nucleophilic anions. We have found that the *p*-toluenesulfonate (14a)¹⁴ and the benzenesulfonate (14b)¹⁵ of 1 are readily prepared by hydrogen peroxide oxidation of 2 in glacial acetic acid in the presence of the appropriate sulfonic acid (SCHEME 5) and that these salts can in fact advantageously be utilized for the production of very pure 1 as well as 2.¹⁴

SCHEME 5.



In pursuit of this result we investigated the utilization of an equimolar mixture of **14** and **2** as a phenylselenenium ion transfer reagent. The

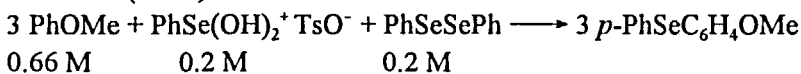
SCHEME 6.



equilibrium involved is symbolized in SCHEME 6. Since protons are liberated during the substitution all three phenylseleno groups can be utilized. The solvent influence on this reagent system was studied by means of model experiments with anisole as the substrate. The results

TABLE 3. Medium dependence of the reagent couple
 $\text{PhSe}(\text{OH})_2^+ \text{TsO}^- / \text{PhSeSePh}$ (**14a-2**).

Reaction (65°C):



Solvent	t (min)	% Conversion of $\text{PhSe}(\text{OH})_2^+ \text{TsO}^-$ ^a
AcOH	15	92
AcOH ^b	15	12
CF ₃ CH ₂ OH	15	91
MeOH	15	33
MeOH	30	45
MeOH ^b	30	13
MeOH, 50% 1,2-dichlorethan	30	45
MeOH, 20% DMSO	30	29
DMSO	30	17
MeOH, 5% H ₂ O	30	5

^a Residual **14a** determined by extraction with base and reduction with hydrazine to **2**. ^b **14a** replaced with an equimolar mixture of **1** and trifluoroacetic acid (TFA).

are shown in TABLE 3. The main conclusion from these results is that the reactivity increases with the acidity of the medium. It is also noteworthy that replacement of the sulfonic acid with the weaker trifluoroacetic acid (TFA) retards the reaction although both acids are sufficiently strong to give complete protonation of **1** (see later). Apparently the active transfer reagent is formed by protonation of a species less basic than **1**, presumably benzeneselenenic acid or a derived species.

Three sets of conditions giving homogeneous reaction mixtures have been applied for preparative purposes: Methanol - 25% dichloromethane at 22°C (**A**), methanol at 65 °C (**B**) and glacial acetic acid at 100°C (**C**). The time needed from complete conversion of anisole into 4-(phenylseleno)anisole under the three sets of conditions is 4.5 days, 4.5 hours and < 3 min, respectively corresponding to an over 2000 fold variation of the reagent reactivity. A series of compounds, (**15**), prepared by these methods are presented in TABLE 4.

The application of the reagent couple **2-14a** to phenylselenenylation of arenes is subject to three sets of limitations: 1) The standard conditions, **A-C**, are not successful with anilines and anilides. Presumably these substrates are oxidized by **14a** present in the equilibrium mixture. 2) Side reactions are encountered under forcing conditions. In method **B** a slow oxidation of the solvent accounts for the reduction of about 7% of **14a** per day. A blank run under conditions **C** showed that 84% of **14a** had disappeared after 2 h. The three lowest molecular weight components of the complex reaction mixture were identified as selenanthrene (**16**) and the oligomeric *p*-phenylene selenides, **17a** and **b** (isolated in 12, 10 and 9% yield, respectively).¹³ These products indicate that unreacted **2** is attacked by the reagent. Thus only substrates more reactive than **2** can

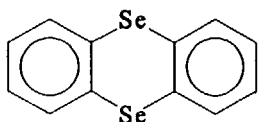
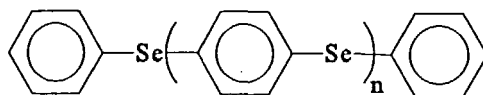
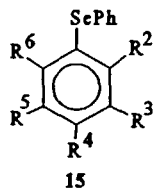
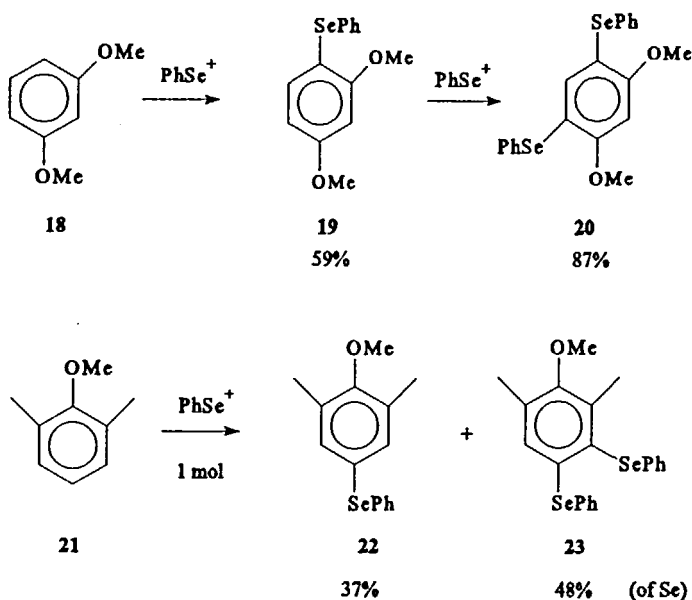
**16****17a: n = 1**

TABLE 4. Phenylselenylation of Arenes with PhSe(OH)_2^+ -
 PhSeSePh .¹³

R ²	R ³	R ⁴	R ⁵	R ⁶	Me- thod	Time (h)	Yield (%)	M.p. (°C) (lit.ref.)
H	H	OH	H	H	A	1.5	73	50-51 ⁹ (52-53 ⁴)
Me	H	OH	H	H	A	1	76	59-60
OH	H	Me	H	H	A	72	35	oil
Me	Me	OH	H	H	A	2	75	72-73
Me	H	OH	H	Me	A	2	76	91-92
Cl	H	OH	H	H	A	20	55	oil
H	CHO	OH	H	H	A	144	59	53-54
H	CO ₂ Me	OH	H	H	C	1	49	41-43
H	H	OMe	H	H	B	4.5	84	40-42 ⁹
H	Me	OMe	H	H	A	72	92	57-58
OMe	H	H	Me	H	B	24	79	70-73 (oil ¹⁶)
Me	H	OMe	H	Me	A	73	79	82-84
H	Br	OMe	H	H	C	0.5	67	87-89
OMe	H	H	Br	H	B	96	66	92-93
Me	H	Me	H	Me	C	1	93	oil

be successfully phenylselenenylated. 3) Alkylarenes are sufficiently reactive to be phenylselenenylated by method C with little accompanying autodestruction of the reagent but the reaction is unsuited for general preparative purposes. The *o-p* selectivity of this class of substrate is low and the regioisomers are not readily separable. The situation is further complicated by the ring-polarization caused by a phenylseleno substituent. The common observation^{4,9} that only a few percent disubstitution accompanies the *p*-phenylselenenylation of phenols and anisols indicates that the phenylseleno group is *m*-deactivating. On the other hand evidence for *o-p* activation is found in the polysubstitution of thiophene^{6,7} and, more clearly by the observation⁷ that 1,2-dimethoxybenzene gives only the 4,5-bis-phenylselenenylated product. In support of these trends we found that phenylselenenylation of 1,3-dimethoxybenzene (**18**) could be controlled

SCHEME 7.



to give either **19** or **20** and that reaction of the sterically hindered 2,6-dimethylanisole (**21**) led to a mixture of mono- and di-substitution products, **22** and **23**, *i.e.* that **22** is slightly more reactive than **21**

(SCHEME 7). Mesitylene with only positions *meta* to the first phenylseleno group available for further substitution gives mesityl phenyl selenide in good yield (TABLE 4). The reaction of toluene leads to an approximately 1:1 mixture of *o*- and *p*-substituted product accompanied by disubstituted products.

Not unexpectedly considering its reactivity toward arenes the reagent **14a-2** is very efficient for phenylselenenylation of more reactive carbon nucleophiles. For example, complete conversion of cyclohexene into 1-methoxy-2-(phenylseleno)cyclohexane (isolated yield 76%)¹³ under conditions **A** required 5 min. The reaction with cyclohexanone (methanol-dichloromethane, 35°C) required 10 min and gave, after bulb to bulb distillation 2-(phenylseleno)cyclohexanone and 2,6-bis(phenylseleno)cyclohexanone (65 and 16 %, respectively, of the available selenium).¹³

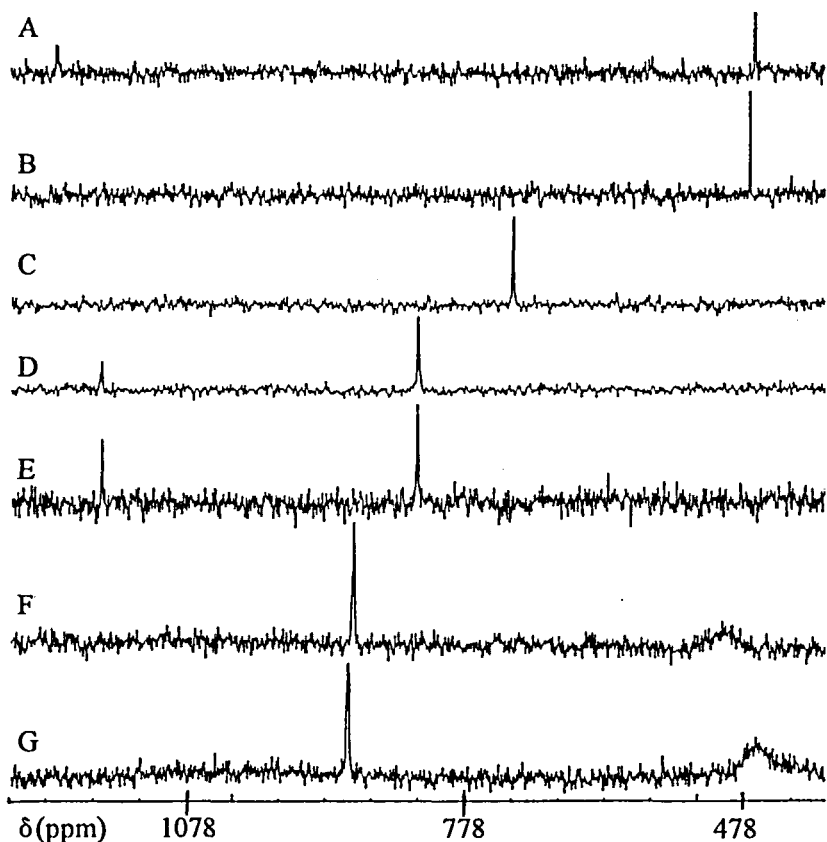
⁷⁷Se NMR SPECTRA OF PHENYLSELENYL-TRANSFER REAGENTS:

⁷⁷Se NMR spectroscopy is a powerful analytical tool for the study of Se-species in solution. We have previously analysed the geometric isomerism in vinylic selenides¹⁷ and the composition of dialkyl polyselenide mixtures.¹⁸ The experimental details of our technique are described in these papers. ⁷⁷Se NMR spectra of **1** and **14a** recorded in various mediae reveals the presence of three species in addition to **1**: Methylbenzeneseleninate (**24**), dihydroxy phenylselenonium ion (**25**) and hydroxy methoxy phenylselenonium ion (**26**). A solution of **1** in DMSO-*d*₆ shows only the

PhSeO ₂ H	PhSe(O)OMe	PhSe(OH) ₂ ⁺	PhSe(OMe)OH ⁺
1	24	25	26
1188	1236	1169	1216 ppm*

*Relative to Me₂Se in CDCl₃; solvent induced effects ± 2 ppm.

FIGURE 1. ^{77}Se NMR spectra: A in Methanol- CDCl_3 (2:3); B-G in TFA- CDCl_3 (2:3).



- A: PhSeSePh (0.32 M) + $\text{PhSe(OH)}_2^+ \text{TsO}^-$ (0.32 M)
 B: PhSeSePh (0.32 M)
 C: PhSeSePh (0.32 M) + PhSeO_2H (0.08M)
 D: PhSeSePh (0.32 M) + PhSeO_2H (0.32M)
 E: PhSeSePh (0.32 M) + $\text{PhSe(OH)}_2^+ \text{TsO}^-$ (0.32M)
 F: Solution E + anisole (0.96 M)
 G: 4-(phenylseleno)anisole (0.96 M) + TsOH (0.32 M)

resonance of **1**. On addition of methanol signals from **1** and **24** are both seen while in MeOH-CDCl₃ only the signal from **24** is recorded. The spectrum of **1** in TFA as well as that of **14a** show the resonances of **25** and **26** in DMSO-*d*₆ and MeOH-CDCl₃, respectively.

FIGURE 1 show a series of recorded ⁷⁷Se NMR spectra. The resonance lines of **2** and **26** are not shifted and only slightly broadened in the spectrum (A) of the reagent couple **14a-2** in MeOH-CDCl₃. A very similar spectrum was recorded of the Tiecco reagent (**2** oxidized with ammonium peroxodisulfate in methanol)⁶ filtered from a precipitate of NH₄⁺HSO₄⁻ and diluted with CDCl₃.

A quite different pattern emerges from the spectra (B-G) recorded in TFA-CDCl₃. The resonance of **2** is undisturbed by TFA (B). Spectra (C-E) all display a signal in the range 800-900 ppm indicating that phenylselenenium ion is generated from **2** with both **1** and **14a**. The variable line width and chemical shift of this signal shows a condition of rapid exchange between **2** and the reactive electrophile (cf. ref.¹⁹). The spectrum (F) of the reaction mixture formed by addition of anisole to reagent **14a-2** as well as that (G) of a solution of 4-(phenylseleno)anisole with added *p*-toluenesulfonic acid show the presence of the same exchange signal around 900 ppm and in addition a very broad resonance from 4-(phenylseleno)anisole displaced 70-90 ppm from that of the undisturbed compound (409 ppm). Spectra F-G indicate an equilibrium situation in which also a relatively fast exchange of the arene-bound phenylseleno group takes place. This result was confirmed by a product analysis. After quenching with water both solutions were found to contain the inserted amount of selenium present as (phenylseleno)anisoles (~90%), **2** (~6%) and **14a** (~3%).

CONCLUSION.

A solution with a stoichiometric composition corresponding to benzene-

selenenic acid, *regardless of its mode of formation*, shows only the separate and sharp ^{77}Se nmr signals of the disproportionation products, **1** (or a species at the same oxidation stage, *e.g.* **24-26**) and **2** when water or other nucleophilic hydroxylic species are present in the medium. Such solutions display the yellow-orange color of **2**. Their reactivities increases with increasing acidity of the medium. Reactions with carbon nucleophiles proceed until the limiting reagent is completely consumed.

Solutions containing measurable concentrations of phenylselenenium ion can be obtained by generating the benzeneselenenic species in dry inert solvents in the presence of a non-nucleophilic counterion (cf. ref.⁸). Alternatively the disproportionation equilibrium can be forced toward production of phenylselenenium ion by the simultaneous application of a strong acid and a perfluorinated co-solvent. A discussion of the effects of perfluorinated solvents on the generation of organic cations has recently appeared.²⁰ Solutions of this type display a ^{77}Se resonance in the 800-900 ppm range corresponding to rapid exchange between **2** and phenylselenenium ion. Their color is more or less deep red.^{5,8,21} The reaction with carbon nucleophiles is fast but reversible and observable concentrations of phenylselenenium ion may be present at equilibrium.

References.

1. T. G. Back, in *Organoselenium Chemistry*, D. Liotta, Ed., John Wiley & Sons, New York, 1987, Chapter 1.
2. T.G. Back, in *The Chemistry of Organic Selenium and Tellurium Compounds, Vol 2*, S.Patai, Ed., John Wiley & Sons, New York, 1987, p 115.
3. K.C. Nicolaou, D. A. Claremon, W. E. Barnette and S. P. Seits, *J. Am. Chem. Soc.* **101** 3704 (1979).
4. P. G. Gassman, A. Miura and T. Miura, *J. Org. Chem.* **47** 951 (1982).
5. G. Lindgren and G. H. Schmid, *Chem. Scripta* **23** 98 (1984).
6. M. Tiecco, L. Testaferri, M. Tingoli, F. Marini and S. Marrigio, *Tetrahedron* **50** 10549 (1994).
7. L. Engman and P. Erikson, *Heterocycles* **43** 861 (1996).

8. a) M. Yoshida, N. Satoh and N. Kamigata, *Chem. Lett.* **1989** 1433; b) M. Yoshida, S. Sasage, K. Kawamata, T. Suzuki and N. Kamigata, *Bull. Chem. Soc. Jpn.* **64**, 416 (1991).
9. L. Henriksen, *Tetrahedron Letters*, **35** 7057 (1994).
10. D. L. Klayman, in *Organic Selenium Compounds*, D. L. Klayman and W. H. H. Günther, Eds., J. Wiley & Sons, New York 1973, p. 105.
11. a) D. H. R. Barton, A. G. Brewster, S. V. Ley, C. and M. N. Rosenfeld, *J. Chem. Soc. Chem. Commun.* **1976** 985; b) D. H. R. Barton, A. G. Brewster, S. V. Ley, C. M. Read and M. N. Rosenfeld, *J. Chem. Soc. Perkin Trans I* **1981** 1473.
12. D. H. R. Barton, J.-P. Finet and M. Thomas, *Tetrahedron*, **44** 6397 (1988).
13. L. Henriksen and N. Stuhr-Hansen, *unpublished results*. New compounds have been characterized by elemental analysis, MS, ^1H and ^{77}Se NMR spectra. Specific preparative and analytical details may be requested by e-mail: larsh@kiku.dk.
14. L. Henriksen and N. Stuhr-Hansen, *Synth. Commun.* **26** 1897 (1996).
15. N. Stuhr-Hansen and L. Henriksen, *Synth. Commun.* **27** 89 (1997).
16. D. H. R. Barton, R. A. H. F. Hui and S. V. Ley, *J. Chem. Soc. Perkin Trans.* **1982** 2179.
17. I. Johannsen, L. Henriksen and H. Eggert, *J. Org. Chem.* **51** 1657 (1986).
18. H. Eggert, O. Nielsen and L. Henriksen, *J. Am. Chem. Soc.* **108** 1725 (1986).
19. L. Henriksen, in *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol 2, S. Patai, Ed., John Wiley & Sons, New York, 1987, p 401.
20. L. Eberson, M. P. Hartshorn, O. Persson and F. Radner, *J. Chem. Soc., Chem. Commun.* **1996** 2105.
21. M. Tiecco, L. Testaferri, M. Tingoli, L. Bagnoli and F. Marini, *J. Chem. Soc., Perkin Trans. I* **1993** 1989.