Novel Se-O and Si-N Bond Metatheses. Mechanistic Probes, Spectroscopic Studies, and Structural Evidence for Reactive Oligomeric Selenoazyl Intermediates

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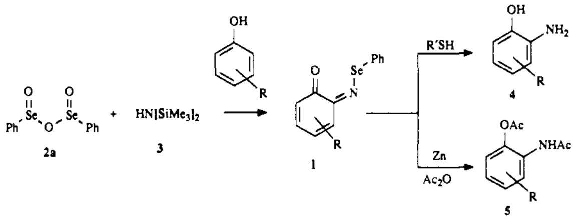
Abstract: Mechanistic studies of the reaction of various seleninic anhydrides and hexamethyldisilazane have provided strong evidence for novel Se-O and Si-N bond metatheses. This reaction produces a reactive intermediate which readily oxidizes a variety of phenols to the corresponding *o*-alkyl or *o*-aryl selenoiminoquinones **1**. The mechanism of this reaction has been identified as a new type of ligand coupling process on the basis of a tetravalent selenium-centered intermediate. The ^{77}Se, ^{29}Si, and ^{15}N NMR studies as well as reactions with pairs of different seleninic anhydrides give good evidence for a hitherto unknown class of cyclic oligomers (eight-membered rings) containing alternate Se-N single and double bonds.

Some years ago we reported a new high-yielding reaction when benzeneseleninic anhydride (BSA, **2a**) was found to react with hexamethyldisilazane (HMDS, **3**) to produce a reactive intermediate which oxidized phenols to *o*-phenyl selenoimines **1**, as exemplified in Scheme I.[1] Relatively few methods are known for the direct and selective oxidation of phenols at the ortho position, particularly when the para position is unblocked. Some recent applications of this reaction, like in the total synthesis of pseudopterosines by Corey and co-workers (where all other methods had failed to give the desired transformation) and in the total synthesis of routiennocin by Ley and others, demonstrate the synthetic utility of this process.[2] Conversion of phenols into phenyl selenoimines **1** represents a mild and convenient procedure for selective ortho amination as the (phenylseleno)iminoquinones **1** can easily be reduced to the aminophenols **4** with thiols. In addition, treatment with zinc and acetic anhydride converts **1** into acetaminophenolic acetates **5**, as shown in Scheme I. The reaction has been tested with several different substrates to further establish its scope and limitations, and it has been found to be very efficient for all the different substituted phenols employed thus far.[1,3] During the course of this reaction, Se-N bond formation takes place and the PhSe≡N moiety is transferred to the phenol. Relatively little[4] is known about the existence or the chemistry of the Se≡N functional group (a logical candidate for the reactive intermediate), and hence we decided to investigate the mechanism of the reaction. Our studies have provided strong evidence for a novel and interesting reaction involving Se-O and Si-N bonds in double metatheses. The first metathesis process leads to the formation of a new class of heterocyclic molecules containing Se-N bonds, followed by the second stage of the metathesis process leading to the products. Furthermore, a new type of tetravalent selenium-centered ligand coupling process has been identified.

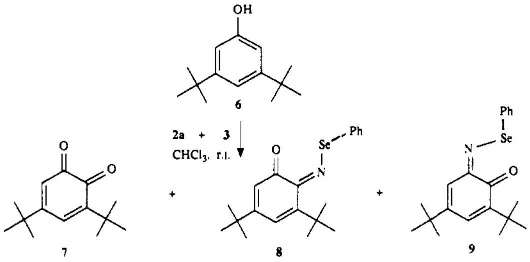
Results

Chemical Evidence. Initially, we chose 3,5-di-*tert*-butylphenol (**6**) as the substrate, as it is symmetrical and also possesses relatively hindered *ortho* positions which would provide a good measure for the efficacy of this reaction for *ortho* oxidation. The product mixture, as shown in Scheme II revealed the presence of compounds **7-9** in different ratios depending upon the reaction conditions employed. The *o*-quinone **7** was found to be produced in much greater amounts when phenol **6** and BSA (**2a**) were mixed first and HMDS (**3**) was added after 30 min of reaction time. The iminoquinone **8** formed in largest amounts when BSA and HMDS were mixed together first and allowed to react for about 30 min and the phenol **6** was added subsequently. The isomeric selenoimine **9** then formed only in small amounts and was completely absent when the phenol was added at a much later stage (after 4 h of reaction time with 12 equiv of HMDS and 1 equiv of BSA). This suggested that different species were responsible for the formation of these three products. The reaction of BSA and HMDS was then carried out in the absence of phenol. During the course of the reaction a gas evolution took place; the gas was later analyzed to be nitrogen.[5] The product mixture showed only diphenyl diselenide and hexamethyl disiloxane. The formations of N_2 and diphenyldiselenide were measured independently with respect to time, and quantitative amounts of Ph_2Se_2 and N_2 (about 98% of the calculated amount) were generated at the end of about 30 h when 2.08 equiv of HMDS (**3**) (with respect to BSA, **2a**) were employed. If larger ratios of HMDS/BSA were employed, the reaction rate was faster. It was clear from the nature of the final products that during the course of this reaction selenium-nitrogen bond formation takes place, providing a reactive intermediate (which contains the PhSeN moiety **10**) which is responsible for the formation of the phenylselenoimine **8** from the

Scheme I



Scheme II



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(1) Barton, D. H. R.; Brewster, A. G.; Ley, S. V.; Rosenfeld, M. N. *J. Chem. Soc., Chem. Commun.* **1977**, 147-148.

(2) (a) Corey, E. J.; Caprino, P. *J. Am. Chem. Soc.* **1989**, *111*, 5472-5474. (b) Kotecha, N. R.; Ley, S. V.; Mantegani, S. *Synlett* **1992**, 395.

(3) Holker, J. S. E.; O'Brien, E.; Park, B. K. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1915-1920.

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(5) The reaction of **2a** and **3** was carried out under an argon atmosphere, and after sufficient amount of gas evolution the gas mixture (above the surface of the reaction solution) was analyzed by GC-MS, showing a peak at 28 *m/e* corresponding to molecular nitrogen.

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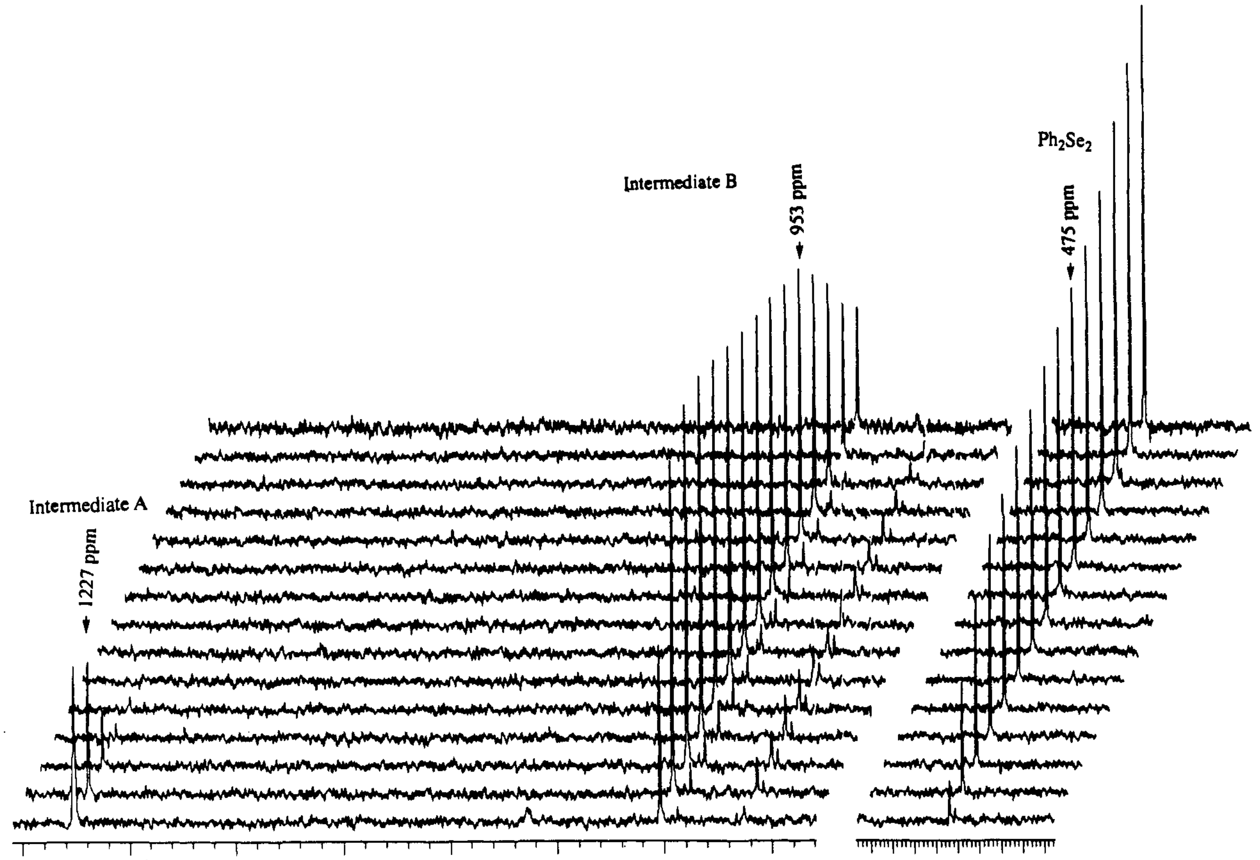


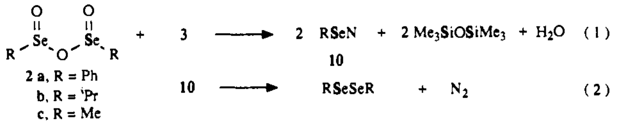
Figure 1. ^{77}Se NMR experiment [BSA (**2a**) (1 equiv) in $CDCl_3$ + HMDS (**3**) (8 equiv) at room temperature]. Diphenyl diselenide was used as an external reference. The time between two spectra is 50 min.

Table 1. Chemical Shift Values[a] of Various Observed Species via NMR

R	Se-77 δ values[b] (and Si-29 δ values[c])					
	$[RSe(O)]_2O$	**A**	**B**	RSeSeR	Me_3SiOH	$[Me_3Si]_2O$
Ph (**2a**)	1241	1227 (26.3)	953	475	(16.0)	(7.1)
^{i}Pr (**2b**)	1314	1298 (26.0)	990	413	(16.0)	(7.1)
Me (**2c**)	1296	1270 (25.8)	910	279	(16.0)	(7.1)

[a] In a typical experiment, 1 equiv of $[RSe(O)]_2O$ was treated with 6 equiv of $HN(SiMe_3)_2$ [δ Si-29 2.4] in $CDCl_3$. [b] Diphenyl diselenide was used as an external referene [δ 475]. [c] TMS was used as an internal referene [δ 0.00].

phenol **6**. Structural evidence of the Se–N bond has been confirmed by the X-ray crystal structure analysis.[6] In the absence of any trap (phenol), this intermediate containing the PhSeN unit reacted further to give PhSeSePh and N_2 (second stage of the metathesis to form Se–Se and N–N bonds). Thus, on a formal basis this reaction can be written as in eqs 1 and 2. A mechanism can be put forward, as shown in Scheme III, which, as we shall show, explains all the facts observed so far.



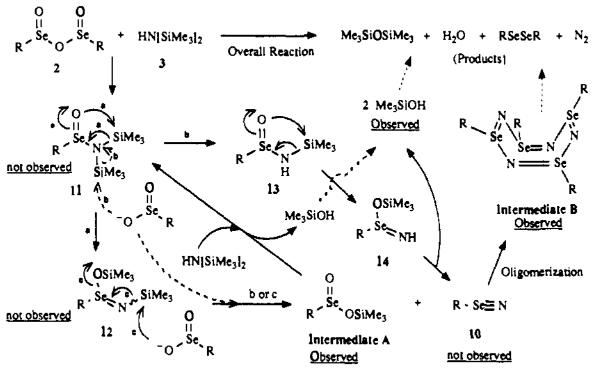
$$[RSe(O)]_2O + 3 \longrightarrow 2\ \underset{10}{RSeN} + 2\ Me_3SiOSiMe_3 + H_2O \quad (1)$$

2a, R = Ph
b, R = ^{i}Pr
c, R = Me

$$10 \longrightarrow RSeSeR + N_2 \quad (2)$$

Nature of the Intermediates: NMR Experiments. We have studied the reaction of **2a** and **3** in the absence of a trapping agent using various spectroscopic techniques. The ^{1}H and ^{13}C NMR studies were uninformative. The ^{77}Se NMR spectra, on the other hand, showed the presence of two observable intermediates **A** and **B** during the course of the reaction, and their corresponding signals eventually collapsed to give the product diphenyl diselenide, as exemplified in Figure 1. Analysis by ^{29}Si NMR also showed two transient species which disappeared over a period of time to give hexamethyldisiloxane. The first intermediate observed via ^{29}Si NMR had the same rate of formation and reaction as the intermediate **A** observed in the ^{77}Se spectra. The second transient species seen in ^{29}Si analysis did *not* have the same rate of formation and reaction as the intermediate **B** observed *via* ^{77}Se NMR. This second intermediate containing silicon was later identified to be Me_3SiOH. When the signal for the intermediate **A** completely disappeared in the ^{29}Si NMR experiments, the only observed species left in the reaction mixture were the hexamethyldisiloxane

Scheme III



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(6) We have done the crystal structure analysis of the selenoimine **8**. The details of the work will be published elsewhere. See also: Atkinson, A.; Brewster, A. G.; Ley, S. V.; Osborn, R. S.; Rogers, D.; Williams, D. J.; Woode, K. A. *J. Chem. Soc., Chem. Commun.* **1977**, 325.

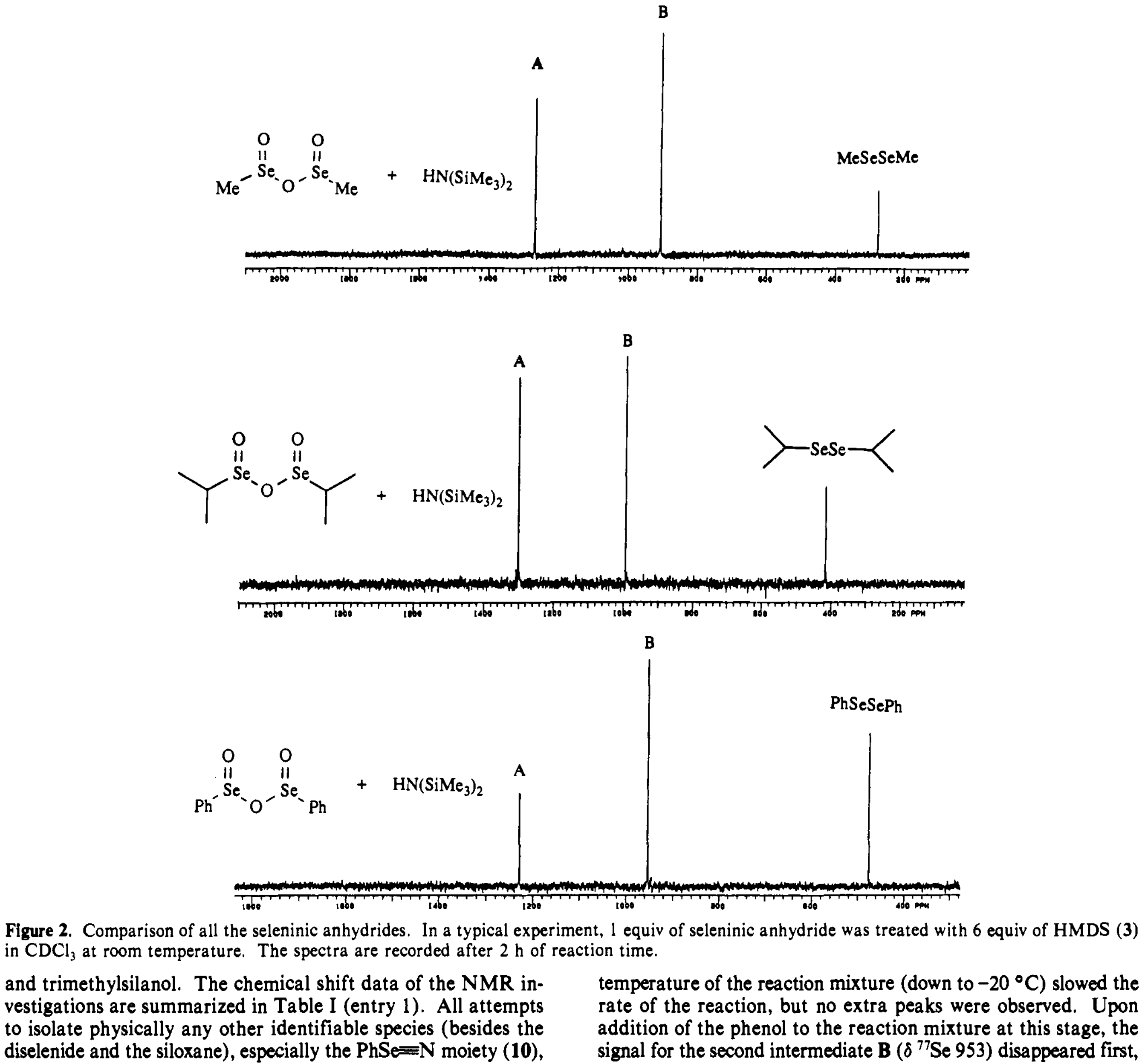

Figure 2. Comparison of all the seleninic anhydrides. In a typical experiment, 1 equiv of seleninic anhydride was treated with 6 equiv of HMDS (3) in $CDCl_3$ at room temperature. The spectra are recorded after 2 h of reaction time.

and trimethylsilanol. The chemical shift data of the NMR investigations are summarized in Table I (entry 1). All attempts to isolate physically any other identifiable species (besides the diselenide and the siloxane), especially the PhSe≡N moiety (**10**), from the reaction mixture failed in our hands. If the PhSe≡N molecule exists as a separate entity, one should expect to be able to capture it by a suitable trapping agent via a cycloaddition reaction. We attempted cycloaddition reactions with various dienes (such as tetraphenylcyclopentadienone and isoprene [4 + 2 cycloaddition]) and dipoles (phenyl azide, dichloromesitylnitrile *N*-oxide, diphenyl nitrone, and diazomethane [3 + 2 cycloaddition]) to no avail. This suggested that the PhSe≡N moiety was unlikely to be stable in a monomeric form.[7]

It was interesting to note that the first intermediate containing selenium appeared to be similar (comparable chemical shifts, see Table I, entry 1) to the starting material BSA in terms of the stereoelectronic environment around selenium.[8] Lowering the temperature of the reaction mixture (down to −20 °C) slowed the rate of the reaction, but no extra peaks were observed. Upon addition of the phenol to the reaction mixture at this stage, the signal for the second intermediate **B** (δ ^{77}Se 953) disappeared first, followed by the signal for intermediate **A** at 1227 ppm, to give rise to stable signals of the products the iminoquinone **8** and the diselenide at 1064 and 475 ppm, respectively.

Additional Structural Probes. We employed two other seleninic anhydrides (*viz.* 2-propaneseleninic anhydride (**2b**) and methaneseleninic anhydride (**2c**)) in a similar manner and observed almost identical results, as exemplified in Figure 2. The chemical shifts of both the transient species in all the three cases were comparable (see entries 1–3, Table I). In the case of the methane- and 2-propaneseleninic anhydrides the ^{1}H NMR spectra during the reaction were not very informative. However, the ^{13}C spectra gave useful information. The ^{13}C spectra also showed two types of alkaneselenyl groups emerging as transient species which eventually collapsed to give the corresponding diselenides. The rates of formation and disproportionation of both these entities were the same as those observed for the two intermediates seen via ^{77}Se NMR experiments.

In all these studies, both of the observed intermediates appeared to be symmetrical entities in terms of the environment around the selenium or the silicon nuclei (magnetic equivalence) even at low temperatures (−20 °C) by NMR measurements. The number of signals did not change. At this stage of the investigations we considered that intermediate **B** was not the monomer PhSeN but probably an oligomer ($(PhSeN)_n$), which, since it showed symmetry (only one ^{77}Se signal), must be cyclic. We considered a

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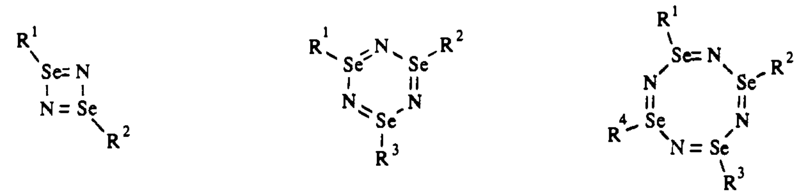
(7) It is likely that dimerization/oligomerization is a more facile process than cycloaddition due to more energetically favorable FMO interaction.

(8) The ^{77}Se chemical shifts are known to have large variations and thereby are highly dependent on the nature of the stereoelectronic environment around the Se and on its oxidation state. See: (a) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: New York, 1986. (b) Nicolaou, K. C.; Petasis, N. A. *Selenium in Natural products Synthesis*; Cis, Inc.: Philadelphia, 1984. (c) Liotta, D. *Organoselenium Chemistry*; John Wiley and Sons: New York, 1987. (d) McFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1397–1401. (e) McFarlane, H. C. E.; McFarlane, W. *Ibid.* **1973**, 2416–2421. (f) O'Brien, D. H.; Dereu, N.; Huang, C.-K.; Irgolic, K. J.; Knapp, F. F. *Organometallics* **1983**, *2*, 305–309. (g) Krief, A.; Hevesi, L. *Organoselenium Chemistry*; Springer-Verlag: New York, 1988.



$R^1 = R^2 = R' \Rightarrow$ 1 signal
$R^1 = R^2 = R'' \Rightarrow$ 1signal
$R^1 = R', R^2 = R'' \Rightarrow$ 2 signals

Total # of signals 4

$R^1 = R^2 = R^3 = R' \Rightarrow$ 1 signal
$R^1 = R^2 = R^3 = R'' \Rightarrow$ 1signal
$R^1 = R^2 = R', R^3 = R'' \Rightarrow$ 2 signals
$R^1 = R', R^2 = R^3 = R'' \Rightarrow$ 2 signals

6

$R^1 = R^2 = R^3 = R^4 = R' \Rightarrow$ 1 signal
$R^1 = R^2 = R^3 = R^4 = R'' \Rightarrow$ 1 signal
$R^1 = R^2 = R', R^3 = R^4 = R'' \Rightarrow$ 2 signals
$R^1 = R^3 = R', R^2 = R^4 = R'' \Rightarrow$ 2 signals
$R^1 = R', R^2 = R^3 = R^4 = R'' \Rightarrow$ 3 signals
$R^1 = R'', R^2 = R^3 = R^4 = R' \Rightarrow$ 3 signals

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Figure 3. Calculation of possible number of signals in a ^{77}Se NMR measurement where the cyclic oligomer was to form *via* random association of RSeN units.

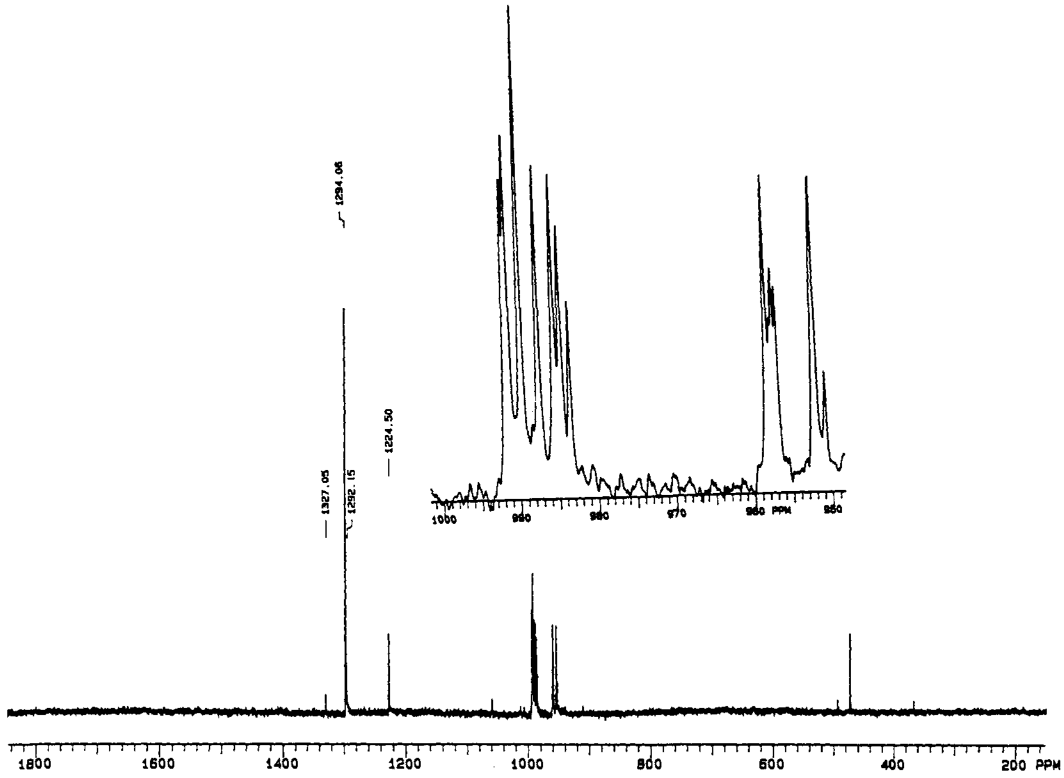

Figure 4. Selenium-77 spectrum of the reaction mixture when benzeneseleninic anhydride (0.5 equiv) + 2-propaneseleninic anhydride (0.5 equiv) were treated with HMDS (12 equiv) in $CDCl_3$ at room temperature.

simple procedure for the evaluation of *n*. It required the further assumption, which was fully justified later by ^{15}N labeling studies, that alternate single and double bonds join the N and Se atoms. Thus the Figure 3 summarizes the number of ^{77}Se peaks that would be seen if two different seleninic anhydrides were mixed, giving rise to a random polymer. For a four-membered ring (dimer), four ^{77}Se signals would be seen, for a trimer, six signals, and for a tetramer, 12 signals. A pentamer, involving two seleninic anhydrides as per same argument (shown in Figure 3), would give 20 ^{77}Se signals.

When benzeneseleninic anhydride (**2a**) and 2-propaneseleninic anhydride (**2b**) were used together in equimolar amounts, 12 major distinct signals were seen (Figure 4) in the ^{77}Se NMR in the 900–1000 ppm range where intermediate **B** normally appeared. However, there were only two peaks at their respective chemical shifts for the corresponding intermediates **A**, and no other additional signals were observed. This was found to be true for any combination of two seleninic anhydrides (of the three listed in Table I). At the end of the reaction, three different diselenides were formed.[9] When a mixture of three seleninic anhydrides was employed, there were a very large number of overlapping signals in the region of 900–1000 ppm. The exact number of signals could not be ascertained, even at higher magnetic field strengths. Nevertheless, the reaction of a mixture of three different seleninic anhydrides with HMDS produced six different diselenides, as was predicted. On the other hand, when mixtures of two or three seleninic anhydrides were employed in reactions with HMDS the ^{29}Si NMR measurements showed no unusual behavior, as two and three signals appeared, respectively, in the region of 26 ppm (instead of one signal in the initial studies when **2a** was treated with **3**). No additional signals resulted (in ^{29}Si NMR) in these mixing experiments. Thus all data are in agreement with the hypothesis discussed above.

^{15}N Enrichment Studies. Further evidence for this hypothesis came from isotopic enrichment studies. We prepared ^{15}N-labeled (99% enrichment) hexamethyldisilazane[10a,b] from $ClSiMe_3$ and

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[9] The relative ratios of all the diselenides formed at the end of the reaction were in full agreement with the relative stoichiometries of the seleninic anhydrides employed.

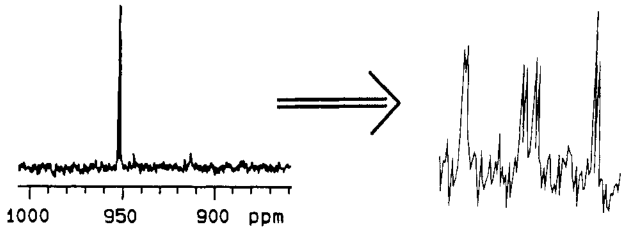


Figure 5. Selenium-77 signal for intermediate **B**, which transformed from a singlet into a doublet of a doublet of a doublet when ^{15}N HMDS was employed.

$^{15}NH_3$. When $H^{15}N[SiMe_3]_2$ was treated with BSA, the signal at 953 ppm, which normally appeared to be a symmetrical species (singlet), now showed three different kinds of Se–N coupling patterns: s → ddd, two $^1J_{Se-N}$ 97 Hz, 84 Hz[10c], and one $^3J_{Se-N}$ 5 Hz, as exemplified in Figure 5. The signal for the intermediate A (in the 1200–1300-ppm region) for all the three seleninic anhydrides showed no change in its appearance. We concluded that the intermediate A contained no Se–N bond. Similarly, ^{29}Si spectra showed no Si–N coupling as the signal at 26 ppm remained unchanged. These observations were consistently true for all the seleninic anhydrides employed. In the ^{13}C spectra the first set of signals of the intermediates A showed no C–N coupling, whereas the second set of peaks (assigned to be that of intermediate **B**) showed two different C–N couplings. These findings support the above conclusions.

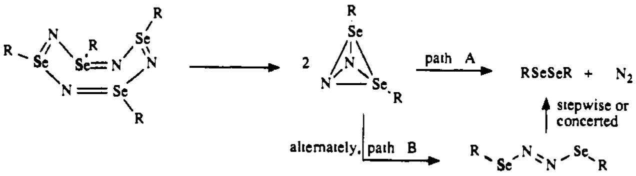
In the ^{15}N NMR measurements the starting material HMDS (δ ^{15}N 29) showed distinct $^1J_{N-H}$ 62 Hz; however, as soon as the seleninic anhydride was added the signal became broad and lost the N–H coupling information. A new signal at 309 ppm grew with respect to time and slowly diminished after reaching a certain concentration level, as can be seen in Figure 6. The N–H coupling became visible again after the intermediate **B** reached its peak concentration and started to diminish. This suggested a rapid exchange of the N–H proton of the HMDS (between various basic sites in the system) at an initial stage of the reaction. The chemical shift of 309 ppm is characteristic of an environment for nitrogen that can be found in phosphazenes.[11] A low-intensity signal also appeared at −2 ppm, as can be seen in the Figure 6. This was identified to be that of $^{15}N_2$, and the signal remained constantly low in intensity and diminished upon purging the reaction mixture with argon.

Other Spectroscopic Analyses. We measured (nitrobenzyl alcohol matrix-assisted) FAB-mass spectra of the reaction mixture at a point where there was a maximum concentration of the reactive intermediates. We found several low-intensity signals at relatively higher *m/e* values (705, 651, 649, 507, 451, etc.). This suggested the possibility of an associative nature of the (phenylseleno)azyl functional group. When dimethylcoumarin matrix-assisted laser desorption (TOF) mass spectroscopy was attempted we saw similar results repetitively. Infrared and UV/vis absorption and Raman (shift) spectra of the reaction were not helpful.

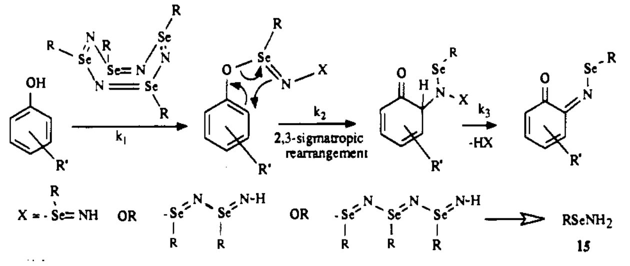
Discussion

The evidence presented above shows that two intermediates can be detected, A and B (Scheme III). These species appear and decay in the presence and in the absence of the phenolic substrate. Intermediate **B** reacts with the phenol to furnish the observed selenoimine **1**. The ^{77}Se signal of intermediate **A** is close to the

Scheme IV



Scheme V



starting seleninic anhydride. When all the intermediate **A** was consumed from the reaction mixture, the ^{29}Si NMR showed the presence of only $Me_3SiOSiMe_3$ and Me_3SiOH. The rates of appearance and further reaction of this intermediate were the same in all the ^{77}Se, ^{29}Si, and ^{13}C NMR measurements. This observation is further supported by the fact that the ^{15}N NMR experiments did not show any signals that could be attributed to the intermediate **A**. This suggested that intermediate **A** has only one RSe and one $SiMe_3$ unit. No Si–N or Se–N couplings were observed for this species in the isotope enrichment studies. The intermediate **A** is also a monomeric unit, as the mixing of different seleninic anhydrides did not change the appearance of the spectra (unlike that of the second intermediate **B**) in terms of the number of signals. Thus there was strong evidence that it was the trimethylsilyl ester of the seleninic acid (Scheme III).

We attempted to synthesize the trimethylsilyl ester of benzeneseleninic acid by an independent route but were unsuccessful. However, we synthesized the triphenylsilyl ester of benzeneseleninic acid ($PhSe(O)OSiPh_3$). The ^{77}Se chemical shift of this derivative was 1296 ppm, and the ^{29}Si chemical shift of it was 21.6 ppm. This was in agreement with the observed values of 1227 (^{77}Se NMR) and 26 ppm (^{29}Si NMR) seen with intermediate **A**.

The rate of appearance of intermediate **B** is dependent upon the relative ratios of BSA and HMDS used. The larger the amounts of HMDS, the faster the rates of formation of intermediate **B** and the faster the rates of disappearance of intermediate **A**. This is in full agreement with the proposed mechanism exemplified in Scheme III. The larger the concentration of **3**, the faster the disappearance of **2**. Thus the larger the concentrations of RSeN, the larger the concentration of the relatively stable cyclic oligomer.

Intermediate **B** is a symmetrical molecule with ^{77}Se signals in the region of 900–1000 ppm. By the method of multiple ^{77}Se signals seen with pairs of mixed seleninic anhydrides, intermediate **B** was shown to be a cyclic tetramer of PhSeN. The ^{15}N NMR chemical shifts of the intermediate **B** indicated an environment for the N similar to the one in cyclotetraphosphazatetraene and/or phosphazanes.[11] In the molecular assembly of the intermediate **B**, three different selenium–nitrogen and two carbon–nitrogen coupling patterns were observed. This suggested that a nonequilibrating (at least on the NMR time scale) alternate double/single bond moiety is indeed present.

The intermediate **B** is not a sufficiently stable species to be isolated. In the absence of any trap it fragments to give the final products. A reasonable mechanism to account for this process is outlined in Scheme IV.

We have carried out in collaboration with Prof. M. B. Hall and Dr. Z. Lin *ab initio* calculations on $[HSeN]_2$, $[HSeN]_3$, and $[HSeN]_4$ treated as cyclic systems. These studies have revealed that the six-membered rings offer all Se–N bonds identical, whereas one of the conformers (boat) of the eight-membered

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(10) (a) Andrianov, K. A.; Kopylov, V. M.; Zaitseva, M. G.; Khan, V. S.; Shkol'nik, M. I. *Zh. Obshch. Khim.* **1979**, *49*, 2683–2689. (b) Cowley, A. H.; Schweiger, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 4179–4185. (c) Duddeck, H.; Wagner, P.; Muller, D.; Jaszberenyi, J. C. *Magn. Reson. Chem.* **1990**, 549–552.

(11) (a) John, A.; Thomas, B.; Pfuetzner, A.; Grossmann, G. *Z. Anorg. Allg. Chem.* **1984**, *511*, 7–18. (b) Thomas, B.; Grossmann, G.; Bieger, W.; Poorzel, A. *Ibid.* **1983**, *504*, 138–146. (c) Thomas, B.; Grossman, G., Meyer, H. *Phosphorus Sulfur* **1981**, *10*, 375–381. See also: (d) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351–358. (e) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101–121. (f) Millington, D.; King, T. J.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1973**, 306–309.

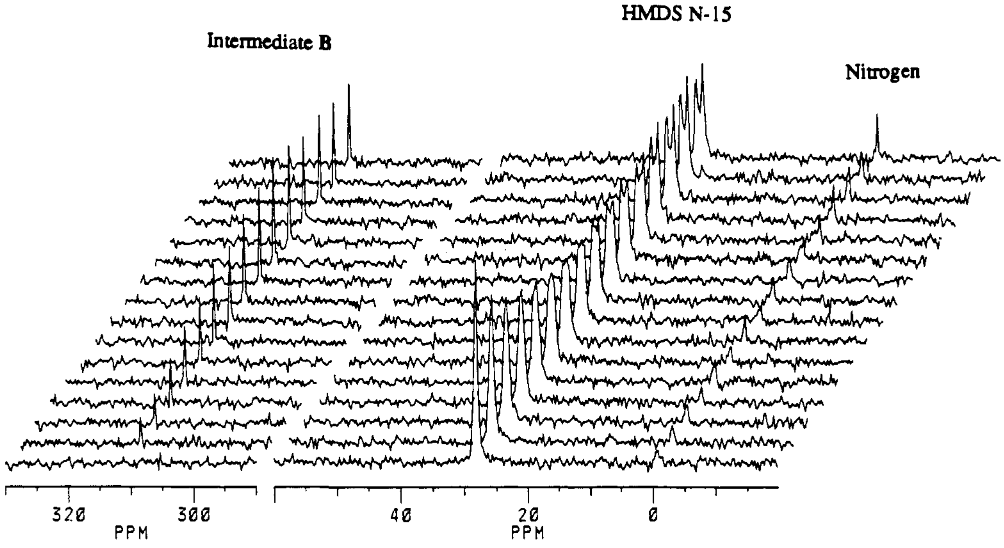
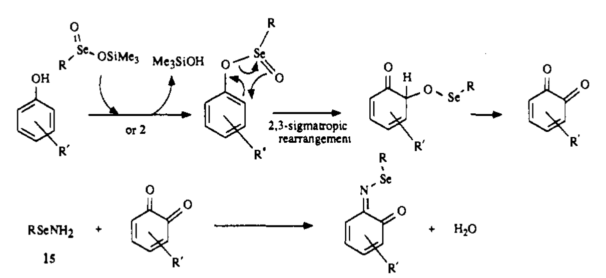
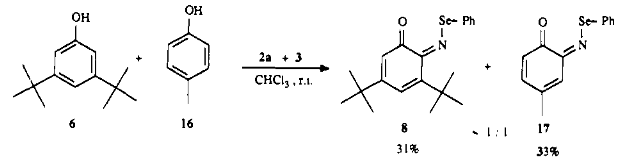


Figure 6. ^{15}N NMR plot of the reaction of **2a** (1 equiv) and ^{15}N hexamethyldisilazene (99% enrichment) in $CDCl_3$ recorded on Bruker 500. Hexamethyldisilazane at 28 ppm. The time between two spectra is 30 min.

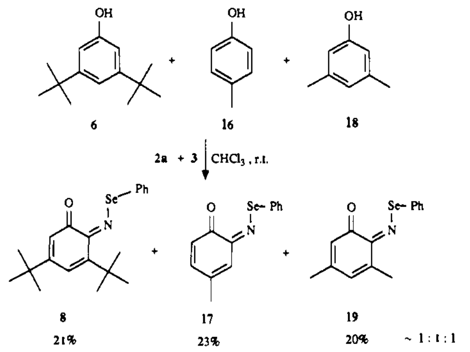
Scheme VI



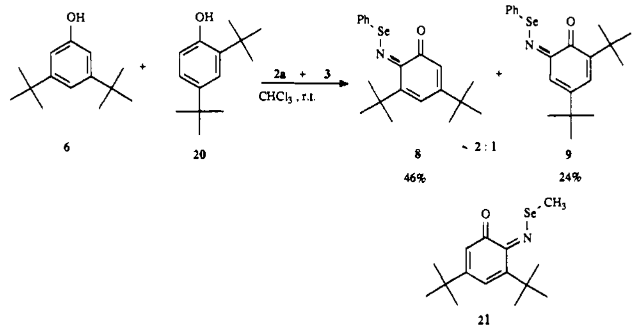
Scheme VII



Scheme VIII



Scheme IX



analogue shows different bond lengths.[12] This is in agreement with the observed differences in the *J* values that we have found.

Intermediate **B** is responsible for the *ortho* oxidation of phenols as it disappears first upon addition of phenol. Any species responsible for this process should provide a mechanism for 2e$^-$ and 2H$^+$ oxidation at the *ortho* position of the phenol before the final formation to the iminoquinone is complete. The tetraalkyltetraselenatetraazene, as depicted in Scheme III as intermediate **B**, does offer a pathway for this condition, as shown in Scheme V. The moiety X in Scheme V could be $(RSe{=}N)_nRSe{=}NH$ [n = 0–2] and would act as a leaving group, finally rendering $RSeNH_2$ (**15**). The selenanamide $RSeNH_2$ can participate in the formation of the isomeric iminoquinone **9** from **7**, as depicted in Scheme VI.

Besides the obvious[13] participation of a seleninic anhydride with a phenol to give the corresponding quinone, the formation of *o*-quinone is also possible *via* the participation of the trimethylsilyl seleninate. The first step of an *O*-selenination followed by a 2,3-sigmatropic rearrangement process, as shown in Scheme VI, would also give a quinone. The fact that intermediate **B** shows such remarkable potential for *ortho* oxidation (facile formation of an iminoquinone from the corresponding phenol), a ligand coupling process (Scheme V) is proposed.

Ligand Coupling Pathways. Having at hand a better understanding of the overall reaction, we decided to further test the scope of this *ortho* oxidation process and our hypothesis of this novel ligand coupling mechanism by employing other substrates. First we attempted to observe additional entities during the oxidation reaction of the phenol, but the reaction was too fast (on the NMR time scale) after the addition of a phenol for anything else to be observed in detectable amounts.

Chemical Evidence. The first step in this ligand coupling pathway should involve an *O*-selenination, and the subsequent step would be a 2,3-sigmatropic rearrangement. The strongest evidence for this hypothesis at a tetravalent Se atom was obtained when we subjected equimolar mixtures of phenols, *viz. p*-cresol (**16**) and 3,5-di-*tert*-butylphenol (**6**) (in 4-fold excess with respect to BSA), to the same reaction conditions. As shown in Scheme VII,

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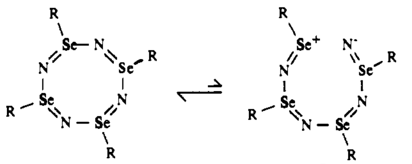
[12] For the details of these theoretical studies: Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh, S. *J. Am. Chem. Soc.*, following paper in this issue.

[13] (a) Barton, D. H. R.; Brewster, A. G.; Ley, S. V.; Rosenfeld, M. N. *J. Chem. Soc., Chem. Commun.* **1976**, 985–986. (b) Barton, D. H. R.; Ley, S. V.; Magnus, P. D.; Rosenfeld, M. N. *J. Chem. Soc., Perkin Trans. 1* **1977**, 567–571. (c) Barton, D. H. R.; Brewster, A. G.; Ley, S. V.; Read, C. M.; Rosenfeld, M. N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1473–1478.

Scheme X



B C

equimolar amounts of the corresponding *o*-iminoquinones **17** and **8** were obtained in 39% and 40% yields, respectively. Similarly, an equimolar mixture of 3,5-di-*tert*-butylphenol (**6**), *p*-cresol (**16**), and 3,5-dimethylphenol (**18**) (in 4-fold excess with respect to BSA) gave the corresponding iminoquinones in equal amounts (28%, 28%, and 26% yields, respectively), as exemplified in Scheme VIII. The reaction did not show any steric dependence.

In order to further establish the nature of the rate-limiting step (intermediate **B** being the limiting reagent), we subjected a mixture of 2,4-di-*tert*-butylphenol (**20**) and 3,5-di-*tert*-butylphenol (**6**) in an equimolar ratio and found the corresponding iminoquinones **9** and **8** formed in the ratio of ~1:2, in 25% and 48% yields, respectively, as illustrated in Scheme IX. This was in agreement with the calculated values on the basis of the number of *ortho* positions available with the starting phenols. Since the phenolic OH in **20** is much more hindered than it is in **6**, it is clear that neither k_1 nor k_2 can be rate limiting. This paradox is simply resolved if the rate-limiting step is the activation of intermediate **B**. This might be activated by bond fission to a very reactive intermediate **c**, not detectable except by its chemical reactivity. Intermediates **B** and **C** might be in equilibrium (Scheme X). An examination of reaction with **6** at -20 °C using ^{13}C NMR did not detect any intermediate on that time scale.

Conclusions

The mechanistic studies of the reaction between **2** and **3** reported here have revealed a novel type of Se–O and Si–N bonds double metatheses whose full synthetic potential is yet to be explored. A new class of ligand coupling process has been identified. One of the most interesting aspects of this mechanism is that very hindered compounds can be synthesized under mild conditions. The chemistry of the Se≡N functional group (self-trapping) and the spectroscopic evidence for eight-membered selenium–nitrogen heterocycles open new avenues of research for this interesting and unusual type of heterocyclic compound.

Experimental Section

General Methods. Melting points were determined with a Kofler hot-stage melting point apparatus and are uncorrected. Proton (chemical shifts referenced to TMS at δ 0.00) and ^{13}C (referenced to CDCl$_3$ at δ 77.00) NMR experiments were carried out at room temperature on a Varian XL-200 or a Gemini-200 spectrometer operating at 200 and 50 MHz, respectively, using 5-mm tubes. Selenium-77 (referenced to Ph$_2$Se$_2$ at δ 475.00) and silicon-29 (referenced to TMS at δ 0.00) NMR measurements were performed on a Varian XL-200 spectrometer operating at 38.2 and 39.7 MHz or on a Varian XL-400 spectrometer at 76.4 and 79.4 MHz, respectively, using 10-mm tubes. Nitrogen-15 NMR studies were conducted on a Bruker 500 spectrometer operating at 50.5 MHz using a 10-mm tube. The solvent used for all the NMR studies was CDCl$_3$.

Infrared (attenuated total reflectance) measurements of the reaction mixtures were carried out using a zinc selenide cell with a Teflon Brand cup containing the solution (of the seleninic anhydride with HMDS in CHCl$_3$) on a Mattson Instruments Galaxy 4021 FT-IR with the MCT detector operating at liquid nitrogen temperature. All the other IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer. The UV/vis spectra were measured with a Beckman Model DU-7 spectrometer.

GC-MS analyses were performed on a Hewlett-Packard 5790A series gas chromatograph equipped with a quadrupole mass-selective detector. Mass spectra were obtained on a VG analytical 70S high-resolution double focusing magnetic sector mass spectrometer with an attached VG 11/250J data system in the EI or FAB mode. The TOF mass spectra were performed using a time-to-digital converter (LeCroy Model 4208 linear) on a Kratos MS-9 electrostatic energy analyzer. All the data acquisition modules were interfaced to an IBM-AT computer using a National Instruments GPIB mainframe card.

Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Solvents were used either as purchased or dried and purified by standard methods.

Dialkyl Diselenides. Diphenyl diselenide was purchased from Lancaster and further purified by recrystallization from hexanes. Dimethyl and diisopropyl diselenides were synthesized according to the literature procedures.[14]

Seleninic Anhydrides. Benzeneseleninic anhydride was obtained from Fluka. Methane- and 2-propaneseleninic anhydrides were synthesized from the corresponding diselenides *via* ozonolysis in dichloromethane at 0 °C. Methaneseleninic anhydride had mp 168 °C.[15] 2-Propaneseleninic anhydride had mp 31 °C. Anal. Calcd. for C$_3$H$_8$O$_2$Se (2-propaneseleninic acid): C, 23.24; H, 5.20. Found: C, 23.18; H, 5.23.

Benzeneseleninic Acid Triphenylsilyl Ester. Triphenylsilyl chloride in dry THF was added to the suspension of the silver salt of benzeneseleninic acid[16] in dry THF at 0 °C in a flask that was pretreated with Me$_3$SiCl to remove surface OH groups, and the solution was allowed to stir under argon atmosphere for 6 h. At the end of the reaction the solids were removed by filtration, and the filtrate was concentrated on a rotary evaporator. The compound melted at 88–90 °C (lit.[16] mp 91 °C).

[^{15}N]Hexamethyldisilazane. Into a stirred solution of freshly distilled chlorotrimethylsilane in anhydrous ether at -78 °C was condensed ammonia-^{15}N (99% enrichment, Isotec, Inc.) *via* a cold finger (dry ice/acetone). The solution immediately turned cloudy, and finely powdered NH$_4$Cl separated. The solution was filtered and concentrated at 0 °C on a rotary evaporator. Pure ^{15}N HMDS was obtained upon distillation at 125 °C (65% yield).

***N*-[2,4-Bis(1,1-dimethylethyl)-6-oxo-2,4-cyclohexadien-1-ylidene]benzeneselenenamide (8).** To a stirred suspension of benzeneseleninic anhydride (1 mmol) in chloroform (15 mL) was added hexamethyldisilazane (12 mmol). The seleninic anhydride slowly went into solution (giving a lightly turbid solution), and slight pink coloration developed. The phenol **6** (1.5 mmol) was added after 30 min of reaction of **2a** and **3**. Immediately after the addition of phenol, deep red color formation took place. After 1 h the reaction mixture was extracted three times with diethyl ether and water. Combined ether layers were washed with saturated NaCl solution and dried over anhydrous Na$_2$SO$_4$. The product mixture was fractionated over silica with a hexanes:methylene chloride solvent mixture in 9:1 ratio as an eluent to give 76% yield of the benzeneselenenamide **8**. ^{1}H NMR (CDCl$_3$) δ: 7.88–7.80 (dd, J = 8.2, 1.2 Hz, 2 H), 7.49–7.40 (m 2 H), 7.34 (d, J = 7.3 Hz, 1 H), 6.8 (d, J = 2 Hz, 1 H), 6.6 (d, J = 2 Hz, 1 H), 1.45 (s, 9 H), 1.28 (s, 9 H). ^{13}C NMR (CDCl$_3$) δ: 178.5, 163.3, 153.3, 148.3, 142.7, 128.9, 128.4, 127.7, 120.1, 118.2, 36.6, 35.9, 30.7, 29.0. ^{77}Se NMR (CDCl$_3$) δ: 1064. IR (film) ν: 3070, 3054, 2954, 2867, 1624, 1591, 1471, 1439, 1023, 983. UV/vis (abs) λ: 446, 206. MS calcd for C$_{20}$H$_{25}$NOSe, 375; found, 375 (M$^+$) 314, 298, 234, 218, 202, 191, 162, 124, 57. HRMS calcd (M$^+$) 375.110 14; found, 375.108 67.

***N*-[3,5-Bis(1,1-dimethylethyl)-6-oxo-2,4-cyclohexadien-1-ylidene]benzeneselenenamide (9).** Reaction of BSA and HMDS as mentioned above also produced 9% yield of the benzeneselenenamide **9** upon isolation. Reaction of the phenol **20** with BSA and HMDS under similar reaction conditions gave 71% yield of **9** upon isolation. ^{1}H NMR (CDCl$_3$) δ: 7.78–7.70 (dd, J = 8.30, 1.42 Hz, 2H), 7.40–7.31 (m, 2 H), 7.25 (d, J = 7.4 Hz, 1 H), 7.18 (d, J = 2.4 Hz, 1 H), 6.84 (d, J = 2.4 Hz, 1 H), 1.30 (s, 9 H), 1.19 (s, 9 H). ^{13}C NMR (CDCl$_3$) δ: 176.8, 155.7, 145.3, 144.6, 141.6, 134.3, 129.0, 128.6, 127.9, 122.2, 35.5, 34.7, 29.3, 29.2. ^{77}Se NMR (CDCl$_3$) δ: 1060. IR (film) ν: 3061, 2964, 2869, 1593, 1476, 1459, 1437, 1260, 1023, 899. UV/VIS (abs) λ: 473, 229, 206. MS, calcd for C$_{20}$H$_{25}$NOSe, 375; found, 375 (M$^+$), 314, 309, 252, 238, 218, 207, 190, 171, 157, 134, 78, 57. HRMS calcd (M$^+$), 375.110 14; found, 375.110 77.

***N*-[3-methyl-6-oxo-2,4-cyclohexadien-1-ylidene]benzeneselenenamide (17).** An authentic sample of the selenoimine **17** was prepared in 64% yield from the reaction of *p*-cresol (**16**) with benzeneseleninic anhydride and HMDS in CH$_2$Cl$_2$ at room temperature. The product upon isolation gave ^{1}H NMR (CDCl$_3$) δ: 7.85–7.77 (dd, J = 8.4, 1.48 Hz, 2 H), 7.49–7.38 (m, 2 H), 7.37–7.28 (m, 1 H), 7.12–7.06 (dd, J = 8.9, 2.1 Hz, 1 H), 6.9 (m, 1 H), 6.68 (d, J = 8.9 Hz, 1 H), 2.13 (s, 3 H). ^{13}C NMR (CDCl$_3$) δ: 177.3, 155.1, 143.2, 141.1, 133.4, 129.0, 128.4, 128.1, 127.7, 125.4, 21.2. ^{77}Se NMR (CDCl$_3$) δ: 1080. IR (film) ν: 3060, 2958, 1627, 1598, 1472, 1433, 1235, 1065, 867. UV/vis (abs) λ: 485, 231.

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MS calcd for $C_{13}H_{11}NOSe$, 277; found, 277 (M^+), 261, 199, 157, 122, 93, 77. Anal. Calcd for $C_{13}H_{11}NOSe$: C, 56.53; H, 4.01; N, 5.07. Found: C, 56.56; H, 3.99; N, 5.06.

***N*-[2,4-Dimethyl-6-oxo-2,4-cyclohexadien-1-ylidene]benzeneselenenamide (19).** An authentic sample of the selenoimine **19** was prepared in 62% yield from the reaction of 3,5-dimethylphenol (**18**) with **2a** and **3** in CH_2Cl_2 at room temperature. The product upon isolation gave ^1H NMR ($CDCl_3$) δ: 7.86–7.79 (dd, $J = 8.38, 1.44$ Hz, 2 H), 7.49–7.40 (m, 2 H), 7.36–7.26 (m, 1 H), 6.43 (m, 2 H), 2.35 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ: 177.7, 154.4, 152.9, 141.9, 137.8, 129.0, 127.8, 127.6, 125.7, 121.8, 22.8, 18.0. ^{77}Se NMR ($CDCl_3$) δ: 1067. IR (CCl_4) ν: 3057, 2967, 2921, 1633, 1594, 1549, 1477, 1444, 1225, 1020, 840, 785. UV/vis (abs) λ: 485, 232. MS calcd for $C_{14}H_{13}NOSe$, 291; found, 291 (M^+), 214, 157, 134, 106, 91, 77. Anal. Calcd for $C_{14}H_{13}NOSe$: C, 57.94; H, 4.51; N, 4.83. Found: C, 57.80; H, 4.52; N, 4.75.

***N*-[2,4-Bis(1,1-dimethylethyl)-6-oxo-2,4-cyclohexadien-1-ylidene]-methaneselenenamide (21).** Reaction of methaneseleninic anhydride (**1b**) with hexamethyldisilazane and 3,5-di-*tert*-butylphenol (added after 1 h of reaction time) under argon gave 67% of the selenoimine **21** upon isolation. ^1H NMR ($CDCl_3$) δ: 6.64 (d, $J = 1.94$ Hz, 1 H), 6.52 (d, $J = 1.94$ Hz, 1 H), 2.73 [s, 3 H (the satellite doublet of 3.69% intensity, $^2J_{Se,H} = 14$ Hz), 1.38 (s, 9 H), 1.21 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ: 178.1, 163.0, 153.9, 147.8, 118.9, 118.4, 36.5, 35.7, 30.6, 28.9, 20.7. ^{77}Se NMR ($CDCl_3$) δ: 1052. IR (film) ν: 2962, 2870, 1623, 1589, 1534, 1441, 1327, 1244, 1180, 1023, 909, 867, 733. UV/vis (abs in $CHCl_3$) λ: 400, 241. MS calcd for $C_{15}H_{23}NOSe$, 313; found, 313 (M^+), 298, 218, 191, 174, 162, 124, 91, 57. Anal. Calcd for $C_{15}H_{23}NOSe$: C, 57.69; H, 7.42; N, 4.48. Found: C, 57.49; H, 7.40; N, 4.47.

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Structure and Bonding in Cyclic Tetrameric Selenium–Nitrogen and Phosphorus–Nitrogen Systems. A Comparative View

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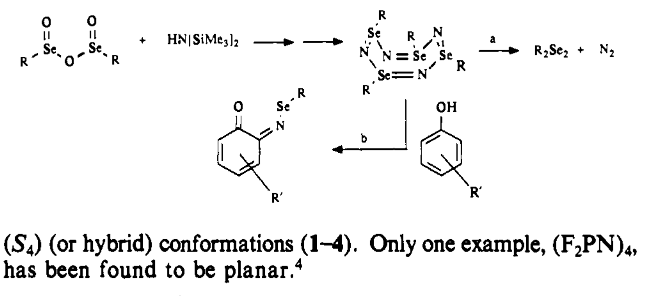
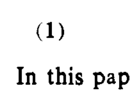
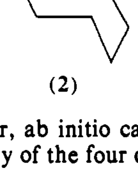
Abstract: Ab initio calculations have been used to study the relative stabilities of various conformations in the tetrameric cyclic $(RSeN)_4$ and $(R_2PN)_4$ systems. The high stability of the "tub" conformer has been rationalized on the basis of electronic and electrostatic interactions. The orientation of the p_π orbitals of the nitrogen atoms is crucial to the stability of these ring systems. Compared to other conformers, the tub conformer allows the maximum number of d orbitals of the Se or P atoms to participate in the π delocalization. Two important differences between the P–N and Se–N ring systems are the stronger ionic character of the Se–N bonds and the steric effect of the Se lone pair.

In the preceding paper, a reactive intermediate was identified in the mechanistic study of the oxidation of phenols to (phenylseleno)iminoquinones by benzeneseleninic anhydride with hexamethyldisilazane, as shown in Scheme I.[1] From extensive NMR evidence the nature of this molecule was determined to be the symmetrical cyclic tetrameric entity $(RSeN)_4$. These cyclic intermediates were found to be very reactive as they disproportionated to the corresponding diselenides and nitrogen gas. It was clear that the factors associated with their assembly, stability, and reactivity needed to be investigated further. Although to the best of our knowledge no structural information can be found on this class of molecules, one can easily relate this intermediate to its phosphorus and sulfur analogues, tetrameric phosphazenes $[(X_2PN)_4$,[2] X can be halide, alkyl, or alkoxyl group] and tetrathiatetraazaenes $(FSN)_4$.[3] Most tetrameric phosphazenes are found in "tub" (S_4), "chair" (C_{2h}), "crown" (C_{4v}), and "saddle" (S_4) (or hybrid) conformations (**1–4**). Only one example, $(F_2PN)_4$, has been found to be planar.[4]

Scheme I




(1)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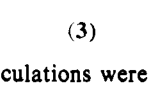
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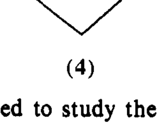
(4)

In this paper, ab initio calculations were used to study the relative stability of the four different conformations mentioned above and to rationalize the structure and bonding in these Se–N

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