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On The Reactions of Benzeneseleninic Anhydride With Monosubstituted Hydrazones. Evidence for Radical Pathways

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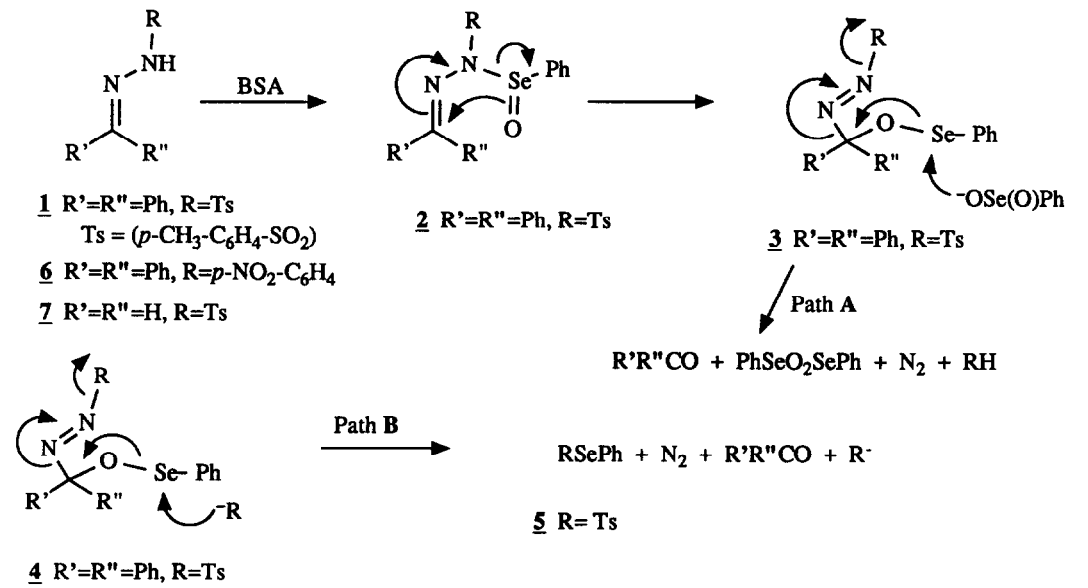
Abstract The known oxidation of mono-substituted hydrazones by benzeneseleninic anhydride has been studied using ^{77}Se and ^{13}C NMR spectroscopy. The intermediates in the reaction have been identified Good evidence that certain steps in these reactions are radical in character has been secured

Benzeneseleninic anhydride (BSA), and the corresponding acid, are useful selective oxidants [1-3] Reoxidation *in situ*[4] reduces the cost of these reagents and affords promising catalytic systems

Some years ago we showed[5] that BSA is an excellent reagent for converting mono-substituted ketone hydrazones back to the ketone The corresponding aldehyde hydrazones gave smoothly acyl azo derivatives, except for aldehyde tosyl hydrazones which were converted rapidly into the parent aldehydes Under the conditions used (room temp) the aldehydes were not oxidized further



1 R'=R"=Ph, R=Ts
Ts = (*p*-CH_3-C_6H_4-SO_2)
6 R'=R"=Ph, R=*p*-NO_2-C_6H_4
7 R'=R"=H, R=Ts

2 R'=R"=Ph, R=Ts

3 R'=R"=Ph, R=Ts

4 R'=R"=Ph, R=Ts

5 R= Ts

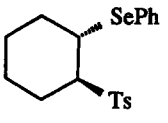
Scheme 1

BSA is a mildly electrophilic oxidant.[3-5] Since electron rich N,N-dimethylhydrazones did not

react with BSA we regarded it as not having electron transfer capacities We ascribed the reactivity towards hydrazones as involving phenylselenination of the -NH function, followed by rearrangement (Scheme 1) Because we were interested in the yield obtained from the carbonyl portion of the starting material we did not look in detail at the other products of the reaction We have now examined in more depth the mechanism of the process.

Since the conversion of tosyl hydrazones back to aldehydes or ketones was a fast high yielding reaction, we studied this transformation first Using the tosyl hydrazone of benzophenone **1** and looking for ^{77}Se signals[6] in $CHCl_3$-C_6D_6, BSA could be seen at 1230 ppm and benzeneseleninic acid at 1190 ppm [7] A major peak at 987 ppm grew with time and was identified as the well known[2] phenylseleno tosylate **5** There was a minor peak at 475 ppm, which did not change much with time. This was identified as PhSeSePh The reaction was far too fast on the NMR time scale to show intermediates **2** and **3**

We had earlier supposed that intermediate **3** was fragmented by (Path A, Scheme 1) the nucleophilic attack of $PhSeO_2^-$, the other half of BSA In light of the formation of **5** the alternative **4** (Path B, Scheme 1) could be considered



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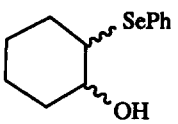

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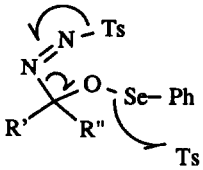

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Now, we reported earlier that BSA oxidation of the *p*-nitrophenyl hydrazone of benzophenone **6** gave nitrobenzene and phenyl-*p*-nitrophenyl selenide These products could well have been from a radical reaction. So we oxidized **1** in the presence of a large excess of cyclohexene. This gave benzophenone as well as **8** in 72% yield and a small amount of **9** The latter is characteristic of the oxidation of cyclohexene by BSA in the presence of some diphenyldiselenide.[8,9] The former is characteristic of radical chemistry [10,11] It is, of course, also produced by the photolysis of **5** in the presence of cyclohexene So we repeated the oxidation of **1** in the presence of excess cyclohexene in the dark The result of the experiment was the same. Hence, we are not dealing with a photochemical radical chain reaction based on **5** We also repeated the same trapping experiment from the oxidation of the tosyl hydrazone of benzaldehyde **7** with the same result

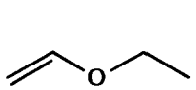
The simplest mechanism to explain these results is that summarized in **10** This is a radical chain reaction We then expanded the scope of the reaction to the other olefins using the tosyl hydrazone **1** The results are summarized in Table 1

Ethyl vinyl ether **11** afforded phenylseleno acetaldehyde **12** (presumably from the hemiacetal **13**, a product of oxidation of the olefinic moiety by BSA)[8,9] as well as the seleno ether **14** and its hydrolysis

Table 1

Entry	Trap	Products (% yields)[a]
1	**11**	**12** (42), **14** (21), **15** (18), Ph_2CO (76), PhSeSePh (28)
2	**16**	**17** (42), **18** (40), **19** (14), Ph_2CO (71), PhSeSePh (30)
3	**20**	**21** (36), **22** (30), Ph_2CO (76), PhSeSePh (30)
4	Ph_2S_2	PhSeSPh (71), $PhSSO_2Tol$ (70), TsSePh (30), Ph_2CO (78), Ph_2Se_2 (12)
5	**24**	**25** (56), $PhSe(CH_2)_2Ph$ (41), TsS-2-Py (39), Ph_2CO (61), Ph_2Se_2 (10)

a = yields mentioned here were based on the integral values from NMR or isolated when it was possible



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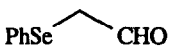

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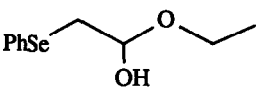

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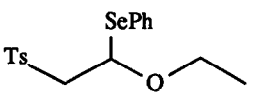

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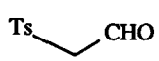

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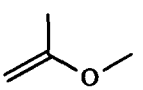

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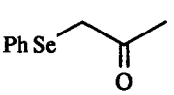

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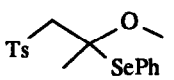

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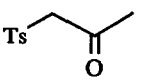

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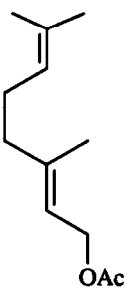
product **15** Diphenyldiselenide was a minor product Benzophenone was reformed in good yield The vinyl ether **16** behaved in a similar manner and afforded phenyl seleno acetone **17** as well as adduct **18** Geranyl acetate **20** gave an adduct **21** along with the elimination product **22** There was no indication of reaction at the allylic double bond. The use of diphenyl disulfide as a trap confirmed the radical nature of the mechanism Thus $PhSSO_2$-*p*-Tol was a major product as well as PhSeSPh Minor products were **5** and $(PhSe)_2$ These results show that the major reaction path was as in **23**

Finally, the acyl derivative **24** was examined as a radical trap (Table 1, entry 5) BSA is well known to convert the thio-carbonyl function into carbonyl [12] Not surprisingly a major product was the amide **25** However, $PhSeCH_2CH_2Ph$ was also formed in good yield and this comes from the radical reaction in **26**, as does another major product *p*-Ts-S-2-Py One can envision the addition of β-phenylethyl radical to



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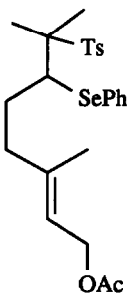

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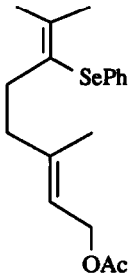

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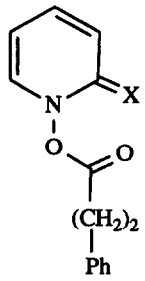
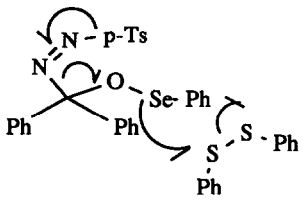


24 X = S

25 X = O



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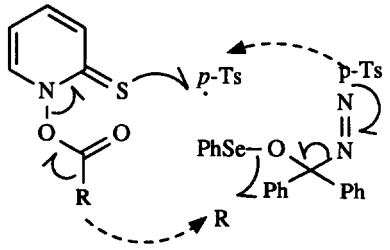

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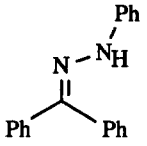
R = CH_2CH_2Ph

diphenyldiselenide (formed during the course of the reaction) to explain the formation of $PhSeCH_2CH_2Ph$ However, when the reaction was carried out in the absence of light it gave comparable yields of products



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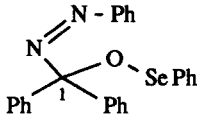

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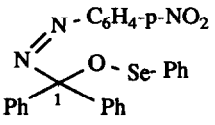
$PhSeCCl_3$ $PhSeCHCl_2$

29 **30**



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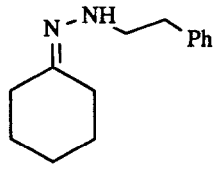

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We also investigated the BSA oxidation of aryl and alkyl hydrazones of ketones (Table 2) The

reactivity of 27 and 6 with BSA was considerably lower than that of 1 and 7, hence, it was possible to study the reaction using ^{13}C NMR. When 27 was treated with BSA in $CDCl_3$ we observed that a signal due to C-1 of 27 at 172 ppm in the ^{13}C NMR collapsed and a new signal at 96 4 ppm appeared. This signal was identified to be that of C-1 in 28 (an sp^3 carbon bonded to N and O) The signal at 96 4 ppm extenuated after a certain time and a new signal at 196 3 ppm emanated. This was identified by comparison with an authentic sample to be benzophenone. The rest of the spectrum was rather uninformative as all the carbon signals were in the aromatic region. We investigated this reaction via ^{77}Se NMR We observed that two initial signals at 1230 and 1189 ppm (BSA and benzeneseleninic acid respectively) attenuated with time and two new signals at 1054 ppm (major) and 475 ppm (minor) appeared The peak at 1054 ppm was attributed to 28 The signal at 475 ppm was due to Ph_2Se_2 The peak at 1054 ppm collapsed after some time to give two additional signals, one at 419 ppm (major) and one at 938 ppm (minor) The signal at 419 ppm was confirmed to be that of Ph_2Se from an authentic sample The peak at 938 ppm was due to minor amounts of $PhSeCCl_3$ 29 formed during the course of the reaction The presence of 29 is good evidence for a radical pathway [13] We carried out the reaction of 27 with BSA in CH_2Cl_2 and also observed $PhSeCHCl_2$ 30 formation (12% yield) along

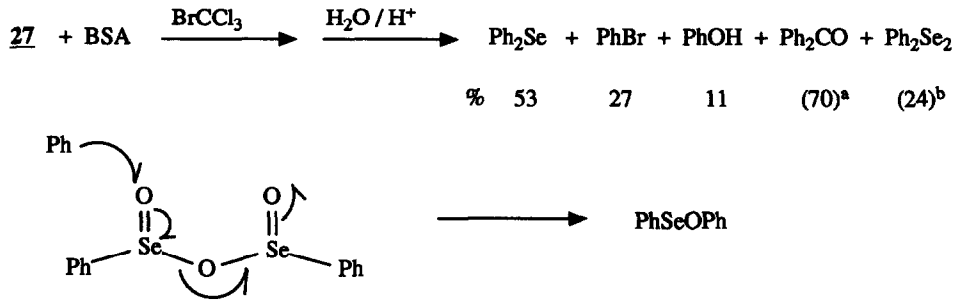
Table 2 [a]

Entry	Hydrazone	Products (yields)[b]
1	27	Ph_2CO (72), Ph_2Se (62), Ph_2Se_2 (43), 29 (14)
2	6	Ph_2CO (69), *p*-NO_2-C_6H_4SePh (58), Ph_2Se_2 (44), 29 (15), $C_6H_5NO_2$ (16)
3	32	35 (74), 36 (76), Ph_2Se_2 (41)
4	38	40 (48), 36 (75), Ph_2Se_2 (45)

a = In a typical experiment 1 equivalent of hydrazone was treated with 1 equivalnent of BSA in $CHCl_3$ as solvent, at r t
b = Yields mentioned here were based on NMR or GC analysis and isolated when possible

with Ph_2CO and Ph_2Se in good yields Diphenyldiselenide was formed in moderate amounts We were unable to get good mass balances for the phenyl moiety as some of the phenyl group was being transformed into benzene during the course of the reaction Hence, we carried out the reaction in $BrCCl_3$ as solvent Because BSA is not very soluble in $BrCCl_3$ the rate of the reaction was a little slower but we obtained an excellent mass balance The mass balance (91%) of only the phenyl moiety of 27 is accounted for by the formation of diphenylselenide, (where only one phenyl group is used for the calculation) bromobenzene and phenol as shown in Scheme 2

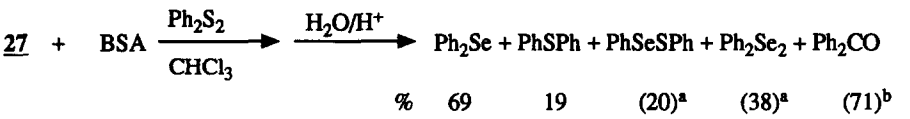
The formation of small amounts of phenol is conceived to be due to attack of phenyl radical at the oxygen of BSA as depicted in Scheme 2 ^{13}C NMR studies of 6 with BSA in $CDCl_3$ gave similar results A



a = based on the starting material benzophenone
b = based on benzene seleninic anhydride

Scheme 2

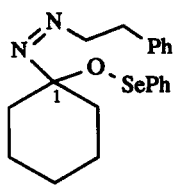
signal at 178 ppm (C-1 in **6**) diminished with time to give a new signal at 96 4 ppm This was assigned to the C-1 in **31** which collapsed and a new signal at 196 3 ppm emanated The peak at 196 3 ppm was due to formation of benzophenone as characterized by an authentic sample In this case we were able to see formation of nitrobenzene and **29** in minor amounts This reaction when performed in CH_2Cl_2 also gave **30** and nitrobenzene in comparable yields (10-15%) This strengthened our working hypothesis of radical fragmentation of **28** and **31** However, any attempts to trap these aryl radicals using olefinic moieties were seriously impaired by a stronger competitive oxidation reaction of the carbon-carbon double bond by BSA to give β-phenylseleno alcohols and/or α-phenylseleno ketones.[3] Diphenyl disulfide proved to be a useful trap as cross coupled products were observed The mass balance of the phenyl group of **27** is explained in the formation of diphenylselenide and diphenylsulfide (by considering the phenyl moiety of **27** only) as shown in Scheme 3



a = based on the benzene seleninic anhydride
b = based on the starting material benzophenone

Scheme 3

Reaction of hydrazone **32** with BSA in $CDCl_3$ was studied via ^1H and ^{13}C NMR spectroscopy ^1H NMR showed that within five minutes two triplets (δ= 3 40 and 2 87 ppm) of the starting material **32** disappeared and a set of new triplets emerged at 4 19 ppm and 3 11 ppm These new signals were assigned to the intermediate **33** Decomposition of **33** was relatively slow (≈70 hrs) Collapse of the two triplets at 4 19



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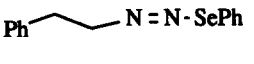

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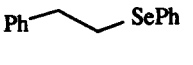

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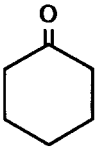

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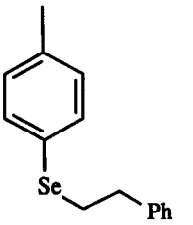

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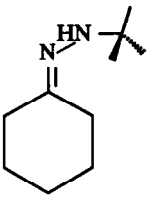

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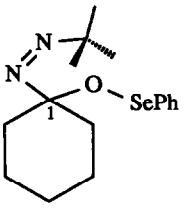

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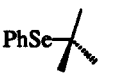

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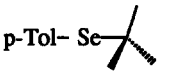

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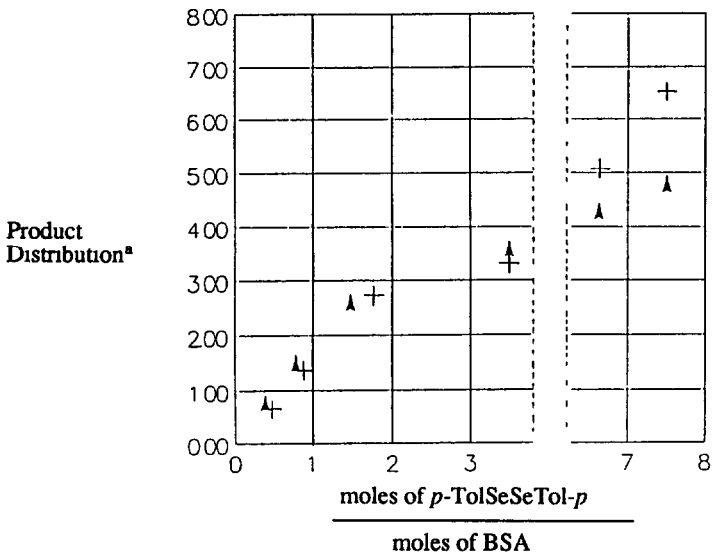
ppm and 3 11 ppm gave new signals A set of triplets at 3 87 ppm and 2 88 ppm attributed to that for **34**, and a triplet (2 95 ppm) and a multiplet (3 12 ppm) characterize for **35** We have compared these data with those for an authentic sample of **35** Now, interestingly the mechanism by which azoalkanes lose nitrogen has been debated for a long time [14] Two mechanisms have received the most attention simultaneous cleavage of both the C-N bonds or stepwise homolysis via a diazenyl radical formation Experimental evidences[15,16,17] and MNDO calculations[18] have shown that stepwise homolysis is a predominant pathway for the photochemical or thermal fragmentation of azo alkanes In our present study the formation of **34** can be viewed in the light of stepwise cleavage of the C-N bond of the intermediate **33** (aided by the α C-O bond) leading to the formation of β-phenylethyl diazenyl radical, which would then carry out the chain process mentioned above ^{13}C NMR studies of this reaction in $CDCl_3$ showed that the signal for the imino carbon at 156 ppm extenuated to give a new signal at 94 6 ppm This new peak was assigned to **33** (C-1) This signal diminished very slowly and a new signal emerged at 210 ppm for **36** ^{77}Se NMR spectral data showed that two initial signals at 1230 ppm and 1189 ppm (for BSA and benzeneseleninic acid respectively) attenuated and two new signals at 1004 3 ppm and 475 ppm appeared The signal at 1004 3 ppm was identified to be for **33** (a divalent 'Se' bonded to oxygen) and the peak at 475 ppm was due to Ph_2Se_2, an inevitable by-product in all these reactions The signal at 1004 ppm attenuated with time to give two additional entities appearing at 834 ppm and 316 ppm The signal at 834 has been assigned to **34** and the one at 316 ppm is confirmed to be that for **35** from an authentic sample The signal at 834 ppm extenuated in intensity slowly over a period of time and the peak at 316 ppm (for **35**) became bigger The cyclohexanone formed in this reaction was in very good yield An interesting observation has been made that supports our rationale for the presence of **34** The ^{1}H and ^{13}C NMR of the reaction carried out at higher temperature (55 ^{0}C), showed complete absence of the

intermediate **34**, and **35** was the only product formed from **33**

Again trapping experiments using olefinic moieties were complicated by the competitive pathway of olefin oxidation by BSA However di-*p*-tolyl diselenide proved to be quite useful to determine the presence of any radicals generated in this reaction We have carefully examined the product distribution using GC and GC/MS studies The amount of ditolyl diselenide was varied keeping the relative amounts of the hydrazone and BSA the same The results plotted in Figure 1, showed that the higher the concentration of trap $(p\text{-TolSe})_2$ (abscissa), the larger the amounts (ordinate) of trapped product **37** formed This provided very strong evidence for a radical chain mechanism for the collapse of the intermediate **33**

Figure 1



a + denotes molar ratio of $p\text{-TolSeCH}_2\text{CH}_2\text{Ph}$ / $\text{PhSeCH}_2\text{CH}_2\text{Ph}$,
▲ denotes molar ratio of $p\text{-TolSe}^t\text{Bu}$ / PhSe^tBu

The reaction of the *tert*-butylhydrazone of cyclohexanone[19] **38** with BSA was studied by ^{77}Se NMR In $CHCl_3$-C_6D_6 the reaction mixture initialy showed the expected BSA (1236 ppm) and the corresponding acid (1189 ppm) These signals attenuated with time to give three new signals at 976 ppm, 536 ppm, and 475 ppm (Ph_2Se_2) The peak at 976 ppm is assigned to the divalent 'Se' in **39** The signal at 536 ppm was identified to be that of *tert* -butylphenyl selenide **40** This has been separated and duly characterized for confirmation The peak for **40** grew taller as the signal for **39** attenuated and disappeared completely We were unable to get good mass balances for the *tert*-butyl group, as the yields of all the identifiable products containing *tert*-butyl were not satisfactory (40-50%) We studied this reaction via ^{1}H NMR We

saw that in $CDCl_3$ a singlet (1 24 ppm) of the starting material shifted downfield (1.3 ppm) which also collapsed and a new singlet appeared (1 4 ppm) The relative integral values of the ^{t}Bu group decreased suggesting a loss of possibly *iso*-butylene gas The ^{13}C NMR showed that in $CDCl_3$ a signal at 150 3 ppm for the imino carbon of **38** collapsed and two new signals at 210 9 ppm and 93.4 ppm emerged The peak at 93 4 ppm has been assigned to the intermediate **39** and the peak at 210 9 ppm was confirmed to be that of cyclohexanone. The signal for **39** attenuated with time and the signal for **36** grew bigger The trapping experiments with ditolyl diselenide gave evidence for the radical nature of the reaction as well as providing a much better mass balance for the ^{t}Bu moiety The results of product distribution against relative amounts of trapping agent monitored by GC are plotted in figure 1 In the ^{77}Se NMR studies of the reaction in the presence of ditolyl diselenide ($CHCl_3$-C_6D_6) two additional signals at 524 ppm and 483 ppm stood out besides the ones mentioned above The signal at 524 ppm was confirmed to be for *tert*-butyl-*p*-tolyl selenide **41** and the one at 483 ppm was due to phenyl-*p*-tolyl diselenide

In conclusion this work confirms the first step in the already proposed mechanism for the oxidation of hydrazones by BSA It reveals also that the final products are produced in radical chain reactions These have potential value for the generation of aryl radicals

Experimental:

^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz respectively with a Varian XL 200 and Gemini 200 spectrometers. Chemical shifts are in ppm and referenced to TMS Coupling constants are in Hz ^{77}Se NMR spectra were recorded at 76 3 MHz with a Varian XL 400 spectrometer The chemical shifts are in ppm where Ph_2Se_2 was either an external or an internal standard (475 ppm) and solvent used was 8 2 $CHCl_3$ C_6D_6 IR spectra were measured with a Perkin-Elmer 881 spectrometer Electron impact (70 eV unless mentioned otherwise) mass spectra were carried out with a Hewlett-Packard 5995c quadrupole GC-MS instrument GC analyses were performed on Chrompack chromatographs Model 439 and 437S. Exact mass measurements were performed with a VG analytical 705 high resolution double focussing magnetic sector mass spectrometer with an attached VG analytical 11/250J data system. The separations on radial thin layer chromatography (Chromatotron) were performed on silica gel 60 (supplied by EM Science, PF-254 containing Gypsum) Melting points were determined on a Kofler hot stage and are uncorrected All solvents and reagents were purified by standard procedures

Preparation of hydrazones

All hydrazones were prepared by literature procedures Hydrazone **32** had ^1H NMR ($CDCl_3$) δ 7 34-7 14 (m,5H), 3 40 (t, J=7, 2H), 2.87 (t, J=-7, 2H), 2.27 (t, J=6 9, 2H), 2 08 (m, 2H), 1 7-1 51 (m, 6H), ^{13}C NMR 151 1, 132 1, 128 8, 128 4, 122 0, 53 6, 41 7, 35 3, 26 8, 25 4, 24 5, IR (thin film) ν (cm^{-1}) 3240, 3030, 2950, 1636, 1600, 1450, 1110, 700 Accurate Mass Calcd ($C_{14}H_{20}N_2$) 216 1627, Found 216 1623

Reaction of Benzeneseleninic Anhydride with the Tosylhydrazone of Benzophenone (1).

BSA (200 mg, 0.55 mmol) was added to a stirred solution of **1** (175 mg, 0 5 mmol) in dry $CHCl_3$ (10 mL) at room temp (25 ^{0}C). The resultant mixture was stirred under an argon atmosphere for 1 hr The crude reaction mixture was concentrated on a rotary evaporator. Careful (minimum exposure to light) separation on radial tlc with hexanes CH_2Cl_2 gave Ph_2Se_2 (98 mg) and TsSePh (118 mg), m p 79-80^{0}C (lit [20] 77-79^{0}C) Benzophenone was obtained in 80% (72mg) yield.

Trapping Experiment with Cyclohexene

The above experiment was carried out in the presence of cyclohexene, 20 mol equivalent After evaporation the NMR of the crude reaction mixture indicated that adduct **8** was present in 72% yield. M p 58-60^{0}C (lit [11] 58-59^{0}C) ^{1}H NMR ($CDCl_3$) δ 7.6 (d, J=8 0, 2H), 7 4-7 0 (m, 7H), 3 89 (dt as a quintet, J_1=J_2=3 5, 1H), 3 13 (dt, J_1=J_2=3 5, 1H), 2 45 (s, 3H), 2 2-1 3 (m, 8H), IR (CCl_4) ν (cm^{-1}) 3035, 1310, 1150, MS, m/e 394 (M^+, ^{80}Se) and 392 (M^+, ^{78}Se) The alcohol **9** was found[21] to have formed in 9% yield ^{1}H NMR ($CDCl_3$) δ 7.55 (m, 2H), 7 3 (m, 3H), 4 9 (td, J=8 0,4 1, 1H), 3 2 (td, J=9 0,4.1, 1H), 2 4-1 2 (m, 8H)

Trapping Experiment with Ethyl Vinyl Ether (**11**)

The BSA oxidation of **1** (as described above) was carried out in the presence of 20 mol equivalent of **11** After aqueous work-up (sat NH_4Cl, NaCl and water) and evaporation of solvent the dark brown oil was fractionated on radial tlc to give phenyl seleno acetaldehyde[22] **12** in 42% yield. The selenoether **14** was isolated in 21% yield ^{1}H NMR δ 7 86 (m, 2H), 7 54-7.3 (m, 7H), 4 7 (t, J=6 7, 1H), 3.78 (q, J=7 5, 2H), 3 58 (d, J=6 7, 2H), 2 45 (s, 3H), 1 1 (t, J=7 5, 3H), ^{13}C ($CDCl_3$) δ 138 9, 132.8, 131.4, 129 9, 128 9, 128 6, 127 8, 126 1, 121 0, 89 9, 67 3, 53 4, 21 4, 14 5, IR (thin film) ν (cm^{-1}) 1339, 1149, Accurate Mass Calcd ($C_{17}H_{20}O_3SeS$) . 384.0316, Found 384 0306

p-Toluenesufonylacetaldehyde **15** was formed in 18% overall yield. ^{1}H NMR ($CDCl_3$) δ 9 45 (t, J=3 8, 1H), 7 85 (d, J=8 9, 2H), 7 48 (d, J=8 9, 2H), 3 18 (d, J=3.8, 2H), 2 44 (s, 3H), ^{13}C ($CDCl_3$) 192.3, 139 1, 128 0, 125 9, 121 7, 54 0, 21 4, IR (thin film) ν (cm^{-1}) 3055, 1719, 1350, 1150, 1080, Accurate Mass Calcd ($C_9H_{10}O_3S$) . 198 0351, Found 198 0358

Trapping Experiment with Isopropenyl Methyl Ether (**16**)

Phenylseleno acetone[23] **17** was formed in 42% yield ^{1}H NMR ($CDCl_3$) δ 7 5-7 1 (m, 5H), 3 34 (s, 2H), 2 23 (s, 3H); IR (thin film) ν (cm^{-1}) 1705, MS m/e 214 (M^+), 199, 171, 130, 117, 91, 77 The selenoketal **18** was formed in 40% yield ^{1}H NMR ($CDCl_3$) δ 7 8 (d, J=8 8, 2H), 7 6-7 2 (m, 7H), 3 24 (s, 3H), 2 41 (s, 2H), 1.32 (s, 3H), ^{13}C NMR $CDCl_3$) 137 9, 132 0, 131.4, 129 9, 127.8, 126.5, 121 1, 70 2, 56 7, 52 4, 24 8, 20 8, MS m/e (no M^+), 369 (M^+ - 15), 327, 278, 213, 170, 157, 132, 105, 91,77, Accurate Mass Calcd (M^+ -

15 $C_{16}H_{17}O_3SeS$). 369 0082, Found 369 0104

p-Toluenesulfonylacetone **19** formed in 14% yield. ^1H NMR ($CDCl_3$) δ 7 82 (d, J=8 8, 2H), 7 48 (d, J=8 8, 2H), 3 2 (s, 2H), 2.4 (s,3H), ^{13}C NMR ($CDCl_3$) 203 1, 138.6, 128.1, 126.4, 122 0, 59.1, 27 6, IR (thin film) ν (cm^{-1}) 3051, 1706, 1352, 1160, Accurate Mass Calcd. ($C_{10}H_{12}O_3S$) 212 0507, Foumnd 212.0510

Trapping with Geraniol Acetate (20)

The adduct **21** was isolated in 36% yield ^1H NMR ($CDCl_3$) δ 7.82 (d, J=8 75, 2H), 7 55-7 18 (m, 7H), 5 10 (m, 1H), 4 45 (d, J=7 2, 2H), 2.3 (s, 3H), 3 09 (m, 1H), 2 26-1 83 (m, 4H), 1 56 (d, J=1 6, 3H), 1 32 (s, 3H), 1 29 (s, 3H), ^{13}C NMR ($CDCl_3$) 171.3, 142 9, 138 0, 131 7, 129 6, 128 0, 127 8, 126 1, 123 3, 120 4, 71.7, 57 6, 39 4, 31.4, 28.9, 25 6, 20 9, 17 6, 16.2, IR (thin film) ν (cm^{-1}) 3031, 1749, 1630, 1595, 1469, 1443, 1345, 1150, 1058, MS m/e (EI 4 6 eV) 508 (M^+ low intensity), 351 (M^+ -157 SePh) and 353 (M^+ - 155 SO_2Tol), Accurate Mass Calcd ($C_{25}H_{32}O_4SeS$) 508 1186, Found 508 1201

6-Phenylseleno geranyl acetate **22** formed in 30% yield ^1H NMR ($CDCl_3$) δ 7.62-7 23 (m, 5H), 5 09 (m,1H), 4 45 (d, J=7.2, 2H), 2 05 (s, 3H), 2 18-1 85 (m, 4H), 1 69 (s, 3H), 1 56 (s, 3H), 1 46 (s, 3H), ^{13}C NMR ($CDCl_3$) 170 9, 141 0, 138 1, 133 6, 130 2, 126 9, 123 1, 121 0, 120.4, 71 6, 40 9, 39 4, 28 9, 26 7, 25 6, 23 7, IR (CCl_4) ν (cm^{-1}) 3035, 1751, 1623, 1471, 1350, 1165, 1063, Accurate Mass Calcd ($C_{18}H_{24}O_2Se$) 352 0942, Found 352.0933

Trapping Experiment with Ph_2S_2

The reaction was carried out as mentioned above with diphenyl disulfide present GC and GC-MS analysis showed that PhSeSPh formed[24] in 71% yield, m p 57-58 °C MS m/e 266 (M^+), 186, 157, 109, 77 $PhSSO_2Tol$ formed[25] in 70% yield, m p 78-80 °C IR (CCl_4) ν (cm^{-1}) 3027, 1597, 1443,1335, 1145, MS m/e 264 (M^+), 218, 184, 155, 139, 109, 91, 65

Trapping Experiment with Anhydride (24)

Upon careful separation the amide (**25**) was isolated[26] in 56% yield M p 76-78 °C. ^1H NMR ($CDCl_3$) δ 7 32-7 15 (m, 6H), 6 71 (m, 1H), 6 15 (m, 1H), 3.11 (t, J=6 5, 2H), 2 95 (t, J=6 5, 2H), ^{13}C NMR ($CDCl_3$) 178 6, 176 1, 140 3, 137 5, 132 8, 131 4, 130 1, 53 3, 35 5, IR (CCl_4) ν (cm^{-1}) 3010, 1805, 1673, 1595, 1532 2-Phenylethyl-phenyl selenide (**35**) was isolated in 41% yield ^1H NMR ($CDCl_3$) δ 7 55 (m, 2H), 7 35-7 13 (m, 8H), 3 16 (m, 2H), 3 02 (m, 2H), ^{13}C NMR ($CDCl_3$) 141 0, 132 6, 130 2, 129 1, 128 5, 128 4, 126 9, 126 4, 36 6, 28 7, MS m/e 262 (M^+), 158, 105, 77, Accurate Mass Calcd ($C_{14}H_{14}Se$) 262 0261, Found 262 0258 *p*-$TolSO_2S$-2-py was formed in about 39% yield ^1H NMR ($CDCl_3$) 8 65 (m, 1H), 7 8 (d, J=8 75, 2H), 7 4-7 1 (m, 5H), 2 4 (s, 3H), ^{13}C NMR ($CDCl_3$) 149 8, 138 2, 135 7, 132 1, 129 4, 123 6, 121 7, 24 7

BSA Oxidation of the Phenyl Hydrazone of Benzophenone (27)

Hydrazone **27** (0 5 mmol) was treated with BSA (0 56 mmol) in $CHCl_3$ (8 mL) under Ar atmosphere At the end of 7 hrs the reaction mixture was subjected to aqueous work up (sat NH_4Cl, NaCl and water) The GC and GC-MS analysis of the crude reaction mixture showed the following product distribution Benzophenone in 72% yield, Ph_2Se 62%, Ph_2Se_2 43% and selenide **29** in 12% yield were obtained. Upon carrying out the reaction in CH_2Cl_2 selenide **30** was formed in 13% yield

In order to verify the presence of **29** and **30**, PhSeNa (from Ph_2Se_2 and $NaBH_4$) in ethanol was treated with $BrCCl_3$ and $BrCHCl_2$ separately to obtain **29** and **30** in 89% and 81% yields Dichloromethyl phenyl selenide **30**, ^1H NMR ($CDCl_3$) δ 7 5-7 2 (m, 5H), 6 76 (s, 1H), MS m/e 240 (M^+), 205, 157, 125, 117, 77, Accurate Mass Calcd ($C_7H_6Cl_2Se$) . 239 9011, Found 239 9015. Trichloromethyl phenyl selenide[27] **30**, ^1H NMR ($CDCl_3$) δ 7 6-7 23 (m), ^{13}C NMR ($CDCl_3$) 143 1, 139 3, 130 0, 129 1, 97 2, MS 274 (M^+), 239, 203, 157, 117, 77, Accurate Mass Calcd ($C_7H_5Cl_3Se$) 273 8593, Found 273 8587

Trapping Experiments with Ditolyldiselenide

The 2-phenylethyl-*p*-tolyl selenide **37** was obtained in varying amounts as Fig 1 shows ^1H NMR ($CDCl_3$) δ 7 55 (d, J=7 9, 2H), 7 4-7 05 (m, 7H), 3 15 (m, 2H), 3 03 (m, 2H), 2 3 (s, 3H) ^{13}C ($CDCl_3$) 141 1, 133 0, 129 8, 129 1, 128 5, 128 4, 126 4, 36 6, 28 7, 20 7, MS m/e 276 (M^+), 262, 158, 105, 91, 77

p-Tolyl-*tert*-butyl selenide **41**, ^1H NMR 7 65 (d, 8 9, 2H), 7 44 (d, 8 9, 2H), 2 3 (s, 3H), 1 4 (s, 9H), MS m/e 228 (M^+), 172, 133, 117, 91, 57, Accurate Mass Calcd ($C_{11}H_{16}Se$) 228 0391, Found 228 0385

Table 3[a]

Selenium-77 Chemical Shift Values[6,28]

Entry	Substrate	δ ppm	Entry	Substrate	δ ppm
1	**5**	987	7	**34**	834
2	BSA	1230	8	**35**	316
3	Ph_2Se	419	9	**39**	976
4	**29**	938	10	**40**	536
5	**30**	668	11	**41**	524
6	**33**	1004	12	PhSe^{t}Bu	483

a = The spectra were typically run in 8·2 $CHCl_3$ C_6D_6 The reference was Ph_2Se_2 (475 ppm) either as an internal or an external standard

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