# Oxidation of 1,1-disubstituted hydrazines with benzeneseleninic acid and selenium dioxide. Facile preparation of tetrazenes

THOMAS G. BACK[1] AND RUSSELL G. KERR

*Department of Chemistry, University of Calgary, Calgary, Alta., Canada T2N 1N4*

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Various 1,1-disubstituted hydrazines were oxidized with benzeneseleninic acid in methanol, generally producing the corresponding tetrazenes in high yield. Studies of the by-products of the reaction, of the effects of protic vs. aprotic solvents, and trapping experiments suggest that *N*-aminonitrenes are unlikely intermediates in this oxidation. An alternative mechanism involving a Pummerer-like reaction of seleninamides derived from the hydrazines is proposed. Tetrazene formation fails when the hydrazine precursor contains an aryl or *p*-toluenesulfonyl substituent, or when it is highly hindered. Selenium dioxide may be employed as the oxidant instead of the seleninic acid, but is generally less efficacious in achieving high tetrazene yields.

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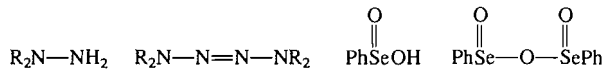
Une variété de hydrazines 1,1-disubstituées a été oxydée par l'acide benzèneséléninique et, en général, de bons rendements des tétrazènes correspondants ont été obtenus. Les études des sous-produits de ces réactions, les effets des solvants protiques et aprotiques, ainsi que le résultat d'une expérience de trappage suggèrent que les *N*-aminonitrénes sont des intermédiaires improbables dans cette oxydation. Un méchanisme alternatif est proposé, dans lequel un séléninamide dérivé de l'hydrazine de départ subit une réaction de Pummerer. La formation des tétrazènes ne réussit pas quand l'hydrazine contient un substituant aryle ou *p*-toluènesulfonyle et également quand l'hydrazine est très encombrée. Le dioxyde de sélénium peut être employé comme agent d'oxydation au lieu de l'acide séléninique, mais la formation des tétrazènes correspondants est généralement moins efficace.

A number of reagents have been employed in the oxidations of 1,1-disubstituted hydrazines **1** to tetrazenes (diaminodiazenes) **2**. Examples include oxides of lead (1, 2), mercury (3–5) and manganese (6), halogens (3, 4), potassium bromate (4), iodate (4) and permanganate (7), lead tetraacetate (8), quinone (2, 9), and *tert*-butyl hypochlorite (10).

Recent studies have shown that benzeneseleninic acid (3) and anhydride (**4**) are efficient oxidants of various hydrazines and hydrazo derivatives (11–13). As an extension of this work, we were prompted to examine the similar oxidation of 1,1-disubstituted hydrazines with **3**. Preliminary results indicated that the transformation of compounds **1** to their corresponding tetrazenes **2** could be smoothly achieved in this manner (14). It is the intent of the present article to further delineate the scope and limitations of this method and to comment on its mechanism. We also describe for the first time several experiments in which selenium dioxide was employed as the oxidant.



**1** **2** **3** **4**

## Results and discussion

The oxidation of hydrazines **1***a*–**1***g* with benzeneseleninic acid **3** in methanol provides tetrazenes **2***a*–**2***g* as the principal products, generally in high yield (see Table 1, entries 1, 6, 10–12, 14, and 16). In most cases the reactions are vigorous and enhanced tetrazene yields were obtained by performing the oxidations at −10°C and by the prompt work-up of the products. The separation of the tetrazenes from diphenyl diselenide and other by-products was readily achieved by preparative tlc. In the case of the relatively insoluble tetrazenes **2***e*–**2***g*, the products crystallized directly from the reaction mixture. This procedure therefore provides a convenient method for the conversion of a variety of 1,1-disubstituted hydrazines to tetrazenes.

Further experiments revealed that a high concentration of both reactants is necessary for optimum results. Entries 2 and 3 in the table reveal that considerable reductions in product yields occurred when either the hydrazine or the seleninic acid was introduced by slow addition. The use of water as solvent instead of methanol in the preparation of **2***a* resulted in only a small reduction in yield (entry 4) while aprotic solvents such as chloroform or diglyme afforded significantly lower yields of **2***b* (entries 7 and 8). Hydrazines **1***f* and **1***g* were oxidized as their sulfates (entries 14–16); an attempt to react the free base of **1***g* with seleninic acid **3** resulted in the recovery of starting material. The low reactivity of the latter compound is in part attributed to its poor solubility in methanol, and may to a large extent be circumvented by employment of the sulfate salt.

[1]Author to whom correspondence should be addressed.

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TABLE 1. Preparation of tetrazenes

| Entry | Hydrazine **1**, $R_2N$ | Oxidant | Yield of **2** (%)[a] | Conditions[b] |
|---|---|---|---|---|
| 1 | **1***a*  | **3** | 74 | Standard |
| 2 | **1***a* | **3** | 39 | Slow addition of **3** |
| 3 | **1***a* | **3** | 7 | Slow addition of **1***a* |
| 4 | **1***a* | **3** | 60 | $H_2O$ solvent, RT |
| 5 | **1***a* | $SeO_2$ | 73 | Standard |
| 6 | **1***b*  | **3** | 78 | Standard |
| 7 | **1***b* | **3** | 40 | $CHCl_3$ solvent |
| 8 | **1***b* | **3** | 43 | Diglyme solvent, RT |
| 9 | **1***b* | $SeO_2$ | 32 | Standard |
| 10 | **1***c*  | **3** | 75 | Standard |
| 11 | **1***d* $Me_2N$ | **3** | 28[c] | Standard |
| 12 | **1***e* $(PhCH_2)_2N$ | **3** | 75 | Standard |
| 13 | **1***e* | $SeO_2$ | 39[d] | RT |
| 14 | **1***f*[e]  | **3** | 96 | Standard |
| 15 | **1***f*[e] | $SeO_2$ | Trace | RT |
| 16 | **1***g*[e]  | **3** | 86 | RT |

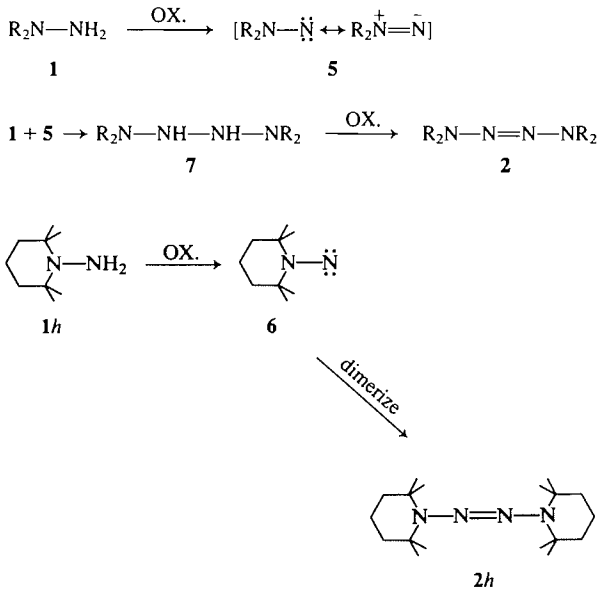
[a]Isolated yield unless otherwise noted.
[b]Standard conditions are described in the experimental section. Any deviations with respect to the mode of addition, solvent, or temperature are indicated in the table. RT = room temperature.
[c]Determined by uv.
[d]Isolated as a mixture with hydrazone **8**; yield determined by integration of the nmr spectrum.
[e]Employed as the sulfate salt.

The use of selenium dioxide in lieu of seleninic acid **3** (entries 5, 9, 13, and 15) was found to give capricious results. For example, *N*-aminopiperidine (**1***a*) gave comparable yields of **2***a* with the two oxidants, while the similar morpholine derivative **1***b* afforded a much lower yield of **2***b* with selenium dioxide. Furthermore, the latter oxidant provided a poor yield of tetrazene **2***e* from **1***e* and failed to react significantly with hydrazine **1***f* even after a longer than normal reaction time at room temperature instead of at −10°C. The use of selenium dioxide also results in the formation of finely divided red selenium as a by-product, which poses additional difficulties during work-up. Consequently, the use of the dioxide in place of seleninic acid **3** is generally not recommended.

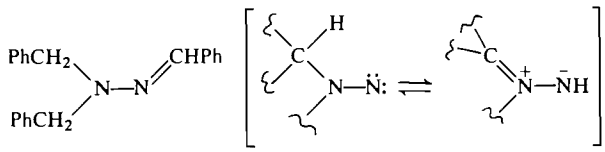
Compelling evidence exists for the formation of intermediate *N*-aminonitrenes (1,1-diazenes) **5** in the oxidations of 1,1-disubstituted hydrazines with certain other reagents such as lead tetraacetate (15). Trapping experiments employing olefins (16, 17) or sulfoxides (16, 18) have resulted in the formation of high yields of *N*-aminoaziridines and sulfoximines, respectively. In the case of the highly hindered and persistent *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**6**), direct characterization by spectroscopic methods was achieved at low temperatures (19–21). Tetrazene formation may result from the further reaction of the aminonitrenes with their precursor hydrazines to produce tetrazanes **7**, which in turn are further oxidized to the final products. In several instances, the tetrazanes have been successfully isolated (22). The direct dimerization of aminonitrenes appears

to be a less common source of tetrazenes, but evidence for such a process has been provided for the dimerization of **6** to tetrazene **2***h* (20). These processes are illustrated in Scheme 1.

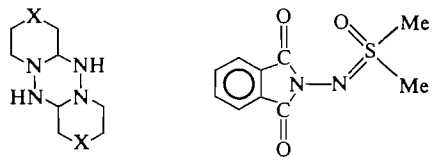
Several of our results indicate that a different mechanism is involved in the present oxidations of hydrazines **1** with **3**. First, the fragmentation of *N*-(dibenzylamino)nitrene to bibenzyl and nitrogen is known to compete favourably with tetrazene formation, frequently providing the major product (6, 9, 10, 23, 24). In contrast, the oxidation of **1***e* with **3** affords no significant amount of bibenzyl, producing instead the tetrazene **2***e* (75%) and hydrazone **8** (22%) as the principal products. Furthermore, aminonitrenes bearing α-hydrogens are capable of tautomerization to the dipolar species **9** (24, 25), a process which is favoured in protic solvents (24). Under such conditions, *N*-piperidino and *N*-morpholinonitrenes are reported to produce cyclic dimers **10**, to the nearly complete exclusion of the corresponding tetrazenes (24). Again, these results contrast with the present system wherein higher yields of tetrazenes **2***a* and **2***b* were produced in protic solvents such as methanol or water than in aprotic solvents such as chloroform or diglyme (see Table 1, entries 1, 4, and 6–8). The trapping of *N*-phthalimidonitrene with dimethyl sulfoxide during the oxidation of **1***g* with **3** was also studied. The sulfoximine **11** had previously been obtained in 74% yield when hydrazine **1***g* was treated with lead tetraacetate in dimethyl sulfoxide (18). However, the present




SCHEME 1




8 9



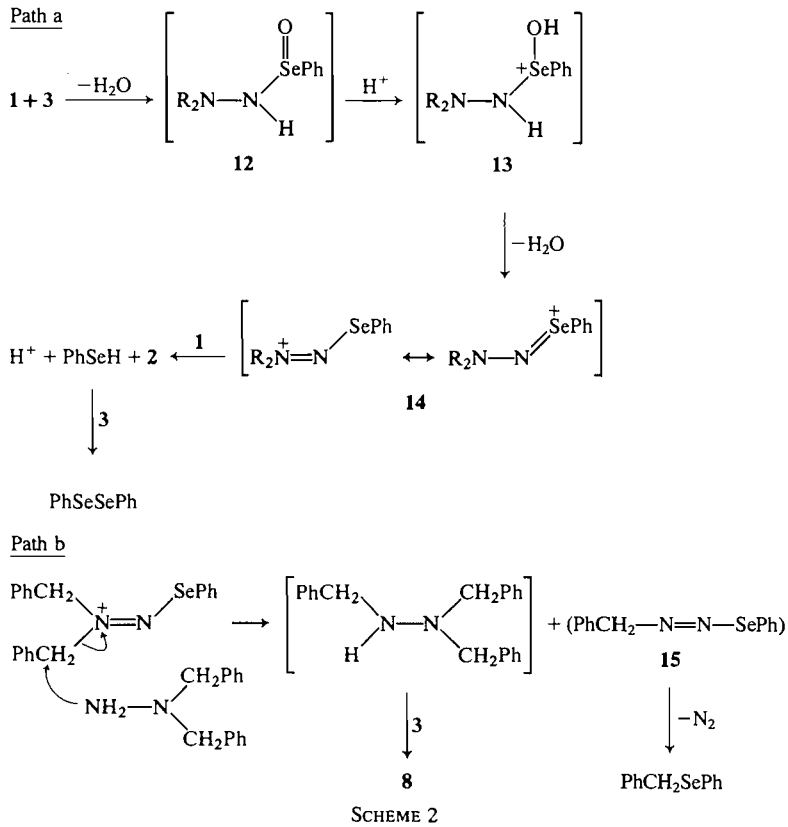

10 X = $CH_2$ or O 11

reaction with **3** afforded the far lower yield of 18% of adduct **11**. These experiments suggest that pathways other than those displayed in Scheme 1 occur in the present oxidations, and that aminonitrene intermediates do not account for a substantial portion of the products obtained.[2]

An attempt was also made to detect the formation of aminonitrene **6** in the oxidation of hydrazine **1***h* with **3**. Since intermediate **6** is known to be stable at −78°C and to possess a deep purple colour (21), its direct observation should be possible if it is produced in the present oxidation at similar temperatures. Unfortunately, the highly hindered parent hydrazine **1***h* failed to react with the seleninic acid below −5°C. At higher temperatures, nitrogen evolution occurred, accompanied by decomposition to a complex mixture of unidentified products. Conclusions regarding the intermediacy of aminonitrene **6** in the present oxidation of **1***h* are therefore precluded.

A plausible mechanism for tetrazene formation which circumvents the need for aminonitrene intermediates is shown in path a of Scheme 2. Seleninylation of **1** with **3** produces seleninamide **12**, resulting in a Pummerer-type reaction catalyzed by the seleninic acid. The Pummerer intermediate **14**

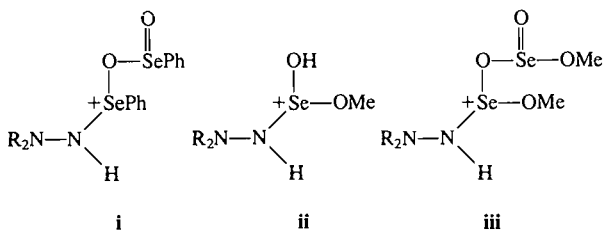
[2]A referee has commented that the evidence for aminonitrene intermediates is not compelling for all reported cases where 1,1-disubstituted hydrazines are oxidized to tetrazenes. We agree that the mechanisms of such oxidations may not be identical in all situations. However, solid evidence for the formation of aminonitrenes has been demonstrated in many of the oxidations cited above, and such species are widely accepted as being common intermediates in these processes. We therefore feel that it is not unreasonable to attribute the observed differences between our results and those in the literature to the fact that the latter reactions involve aminonitrenes as their authors suggest, whereas ours do not.




SCHEME 2

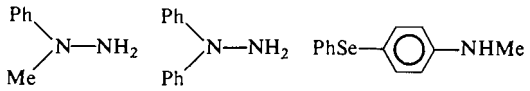
is thus generated via species **13**.[3] The further reaction of **14** with hydrazine **1** then affords the product tetrazene with concomitant formation of benzeneselenol, which is readily oxidized to diphenyl diselenide by the seleninic acid. Related Pummerer reactions of selenoxides have been previously reported (26–32) and seleninic acid **3** is known to be an effective catalyst in these processes (26, 27). The use of polar solvents such as methanol or water may facilitate these transformations by solvation of the ionic intermediates shown in the above scheme. The formation of hydrazone **8** in the oxidation of *N*,*N*-dibenzylhydrazine **1***e* is also consistent with the Pummerer reaction in Scheme 2. The Pummerer intermediate **14** may undergo attack by hydrazine **1***e* at one of the benzylic positions instead of at the *N'*-nitrogen atom (path b), resulting in the formation of tribenzylhydrazine and diazene **15**. Further oxidation of the hydrazine by **3** leads to the observed product **8**, while nitrogen extrusion from **15** provides benzyl phenyl selenide, a small amount of which was also isolated from the reaction mixture. Additional support for these steps derives from literature precedents. The formation of **8** from tribenzylhydrazine closely resembles the oxidation of certain amines with the related oxidants benzeneseleninyl chloride (33) and anhydride **4** (34) to produce imine intermediates. Also, nitrogen extrusions from aryl or acyl analogues of **15** have previously been postulated to account for the observed formation of aryl phenyl selenides and selenoesters in the oxidations of arylhydrazines or hydrazides with **3** (11). The transformations depicted in Scheme 2 are therefore entirely consistent with both the present and previous observations.

[3]The conversion of **12** to **14** could also be achieved by seleninylation rather than protonation of the seleninamide oxygen atom by **3**, resulting in the formation of intermediate **i** in lieu of **13**. Similarly, oxidations performed with methanolic selenium dioxide (dimethyl selenite) could proceed via intermediates **ii** or **iii**.



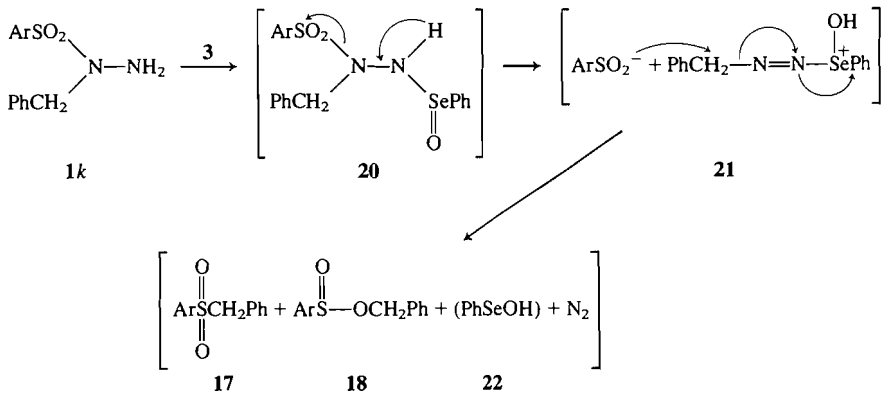

**i** **ii** **iii**

We also report that certain 1,1-disubstituted hydrazines undergo anomalous oxidations with seleninic acid **3**. Thus, *N*-methyl-*N*-phenylhydrazine (**1***i*) afforded a complex mixture which provided *N*-methyl-*p*-(phenylseleno)aniline (**16**) as the only recognizable component. Similarly, the oxidation of *N*,*N*-diphenylhydrazine (**1***j*) produced a mixture containing at least ten components, whose identification was not attempted. It therefore appears that this method is unsuitable for the preparation of tetrazenes bearing aryl substituents.



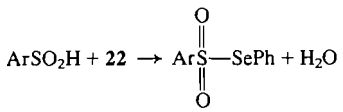

**1***i* **1***j* **16**

The oxidation of *N*-benzyl-*N*-*p*-toluenesulfonylhydrazine (**1***k*) with **3** also proved to be anomalous. When the reaction was performed in chloroform, the principal products were the sulfone **17**, the sulfinate ester **18**, and the selenosulfonate **19**, isolated in yields of 38%, 25%, and 30% respectively, along with diphenyl diselenide. These results suggest that the ambident *p*-toluenesulfinate anion is formed as an intermediate and undergoes either *S*- or *O*-benzylation, or selenenylation to afford the respective products **17**–**19**. Scheme 3 illustrates a possible mechanism in which the elimination of *p*-toluenesulfinic acid from the initially formed intermediate **20** (analogous to **12** in Scheme 2) simultaneously generates the putative benzylating species **21**. The alkylation of the sulfinate anion with the latter (or with benzyldiazonium ion derived from its decomposition) affords the observed products **17** and **18** as well as benzeneselenenic acid (**22**). Any sulfinic acid which escapes benzylation can react with the selenenic acid to furnish the selenosulfonate **19**. A similar reaction has been previously employed by Gancarz and Kice (35) to prepare this selenosulfonate from its corresponding sulfinic acid. The known disproportionation (36, 37) of unreacted selenenic acid accounts for the formation of diphenyl diselenide. A small amount of benzyl phenyl selenide was also produced. Finally, additional evidence for the presence of an electrophilic benzylating agent such as **21** (or the related diazonium species) derives from an analogous experiment performed in methanol. In this case, the nucleophilic solvent effectively competes with the sulfinic acid to produce benzyl methyl ether in 70% yield. The previous benzylation of the sulfinic acid is thus suppressed and it is free to react instead with selenenic acid **22**. Consequently, an enhanced

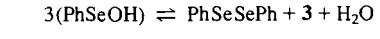



**1***k* **20** **21**

**17** **18** **22**




**19**




SCHEME 3[a]

[a]Ar = *p*-tolyl.

yield of 71% of selenosulfonate **19** is obtained under these conditions.[4]

It is evident that the oxidation of 1,1-disubstituted hydrazines with benzeneseleninic acid, and less reliably with selenium dioxide, provides facile access to a variety of tetrazenes. Anomalous results are expected in those cases where the hydrazine contains aryl substituents, leaving groups such as the sulfonyl moiety, or where it is highly hindered.

## Experimental

*General*

Melting points were determined on an A. H. Thomas hot stage apparatus. Ultraviolet and ir spectra were recorded on a Varian–Cary 219 and a Perkin–Elmer 467 spectrometer, respectively. The nmr spectra were obtained on a Hitachi Perkin–Elmer R24B instrument at 60 MHz or on a Varian XL-200 spectrometer at 200 MHz. All nmr spectra were taken in $CDCl_3$ solution and are reported in ppm (δ) downfield from TMS as the internal standard. Mass spectra were recorded on a Varian MAT CH5 instrument. Elemental analyses were obtained by Mr. L. Malek. Preparative tlc was performed on Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. The gc analyses were carried out on a Varian 3700 instrument equipped with a flame ionization detector and a Varian CDS-111 electronic integrator. Stainless steel columns (1.8 m × 0.3 cm) packed with 10% OV-101 on Chromosorb WHP were used. Benzeneseleninic acid was either purchased from the Aldrich Chemical Co. or prepared from the nitric acid oxidation of diphenyl diselenide according to the method of Barton *et al.* (38). In the latter case, the initially formed nitrate salt was neutralized *in situ* with aqueous NaOH and reprecipitated with concentrated HCl. Literature methods were employed in the preparation of hydrazines **1***e* (39), **1***h* (3), and **1***k* (40). All other reagents were obtained from commercial sources. Diphenyl diselenide was produced in all of the hydrazine oxidations involving **3**, but was only isolated in a few representative examples.

*Preparation of Tetrazenes (see Table 1)*

N,N′-*Bis(piperidino)diazene* (**2**a)

*Under standard conditions*

A solution of *N*-aminopiperidine (**1***a*) (100 mg, 1.00 mmol) in 3 mL of MeOH was cooled to −10°C. Seleninic acid **3** (189 mg, 1.00 mmol) was added in a single portion and the solution rapidly turned yellow from the formation of diphenyl diselenide. After 5–10 min, the reaction mixture was allowed to warm to room temperature and the solvent was promptly removed *in vacuo*. The residue was separated by preparative tlc (20% EtOAc–hexane) to afford 72 mg (74%) of **2***a*; mp 42–43°C (lit. (6) mp 44°C) from EtOH–$H_2O$; identified by its ir and uv spectra (6); mass spectrum, *m/e* 196 ($M^+$).

*By slow addition*

When the seleninic acid in 5 mL of MeOH was added over 40 min (by a mechanically driven syringe pump) to the hydrazine in 3 mL of MeOH at −10°C and worked up as above, the yield of **2***a* was 38 mg (39%). Similarly, slow addition of **1***a* to **3** afforded 7 mg (7%) of **2***a*.

*In $H_2O$*

The reactants were stirred 2 h in 5 mL of $H_2O$ at room temperature. The solution was then extracted with 3 × 5 mL of $CHCl_3$, the combined organic layers were dried ($MgSO_4$) and chromatographed in the usual manner to provide 59 mg (60%) of **2***a*. Gas chromatographic analysis prior to work-up revealed no detectable *N*-nitrosopiperidine.

*With $SeO_2$ as oxidant*

A solution of $SeO_2$ (111 mg, 1.00 mmol) in 1 mL of MeOH was added in one portion to hydrazine **1***a* in 2 mL of MeOH at −10°C. A red precipitate (selenium) rapidly formed. After 5–10 min, the reaction mixture was evaporated to dryness *in vacuo*, triturated with $CHCl_3$, filtered through Celite, and chromatographed in the usual manner. The yield of **2***a* was 72 mg (73%).

N,N′-*Bis(morpholino)diazene* (**2**b)

*Under standard conditions*

*N*-Aminomorpholine (**1***b*) (102 mg, 1.00 mmol) was oxidized with **3** (189 mg, 1.00 mmol) as in the case of **1***a*. Preparative tlc (40% EtOAc – hexane) afforded 78 mg (78%) of **2***b*; mp 153–155°C (lit. (6) mp 157°C) from MeOH; identified by its ir and uv spectra (6); mass spectrum, *m/e* 200 ($M^+$). A more mobile component provided 88 mg of diphenyl diselenide, identified by comparison with an authentic sample (mp, tlc). Attempts to crystallize **2***b* directly from the reaction mixture resulted in contamination with diphenyl diselenide.

*In aprotic solvents*

When the above reaction was repeated in chloroform at −10°C or in diglyme at room temperature, the yield of **2***b* was 40% and 43% respectively.

*With $SeO_2$ as oxidant*

Hydrazine **1***b* (102 mg, 1.00 mmol) was oxidized with $SeO_2$ (111 mg, 1.00 mmol) as described for **1***a*. The yield of **2***b* was 32 mg (32%).

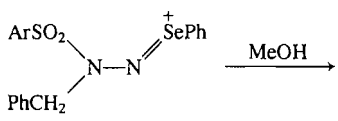
N,N′-*Bis(2,6-dimethylpiperidino)diazene* (**2**c)

*N*-Amino-2,6-dimethylpiperidine (**1***c*) (128 mg, 1.00 mmol) was oxidized with **3** (189 mg, 1.00 mmol) under the standard conditions described for **1***a*. Preparative tlc (25% EtOAc – hexane) afforded 95 mg (75%) of **2***c*, which solidified upon cooling; mp 36–40°C (lit. (5) mp 44–45°C); uv (MeCN), $\lambda_{max}$: 249 nm (ε 9800), 284 nm (sh, ε 2500); ir (film): 1455, 1370, 1320, 1282, 1212, 1110, 1054 $cm^{-1}$; Raman spectrum, 1445 $cm^{-1}$ (N=N); nmr (200 MHz) δ: 3.52 (m, 4H, CH), 1.85–1.4 (complex, 12H, $CH_2$), 1.05 (d, $J$ = 6.6 Hz, 12H, $CH_3$); mass spectrum, *m/e* 252 ($M^+$).

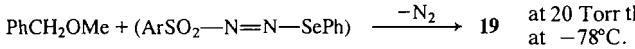
N,N′-*Bis(dimethylamino)diazene* (**2**d)

*N*,*N*-Dimethylhydrazine (**1***d*) (60 mg, 1.00 mmol) was oxidized with **3** (95 mg, 0.50 mmol) under the standard conditions described for **1***a*. Volatile material was distilled, first at 20 Torr then at 0.05 Torr pressure, into a cold trap maintained at −78°C. Ultraviolet analysis of the distillate (lit. (25) uv (MeOH) $\lambda_{max}$: 277 nm, log ε 3.92) indicated the presence of 16 mg

[4]The formation of **19** in methanol solution could also arise from the diazene **v**, in turn derived from the methanolysis of **iv**. However, the formation of **17** and **18** in chloroform solution would be difficult to rationalize from species **iv**. A free radical mechanism for the oxidation of **1***k* cannot be entirely ruled out, but again would not readily explain the formation of benzyl methyl ether in methanol solution.




**iv**




**v**

(28%) of **2***d*. A slightly lower yield was obtained when an equimolar amount of **3** was employed.

N,N′-*Bis(dibenzylamino)diazene* (**2**e)

*Under standard conditions*

*N,N*-Dibenzylhydrazine (**1***e*) (212 mg, 1.00 mmol) was oxidized with **3** (189 mg, 1.00 mmol) as in the case of **1***a*. A white, crystalline precipitate formed within several seconds and was filtered after 10 min to afford 158 mg (75%) of **2***e*; mp 95–98°C (lit. (9) mp 95–96°C); uv (MeOH) $\lambda_{max}$: 287 nm (ε 12 000); ir ($CHCl_3$): 1607, 1497, 1457, 1352, 957, 700 $cm^{-1}$; nmr (60 MHz) δ: 7.12 s, 20H, Ph), 4.30 (s, 8H, $CH_2$); mass spectrum, *m/e* 420 ($M^+$). The filtrate was concentrated and separated by preparative tlc (50% $C_6H_6$ – hexane) to give 33 mg (22%) of hydrazone **8**, mp 81–82°C (from MeOH), identical (mp, ir, nmr) to an authentic sample prepared from **1***e* and benzaldehyde. A more mobile band was rechromatographed (20% $CCl_4$ – hexane) to afford 100 mg of diphenyl diselenide and 6 mg of benzyl phenyl selenide, identified by its nmr and mass spectra.

*With $SeO_2$ as oxidant*

Hydrazine **1***e* (106 mg, 0.50 mmol) and $SeO_2$ (56 mg, 0.50 mmol) were stirred in 3 mL of MeOH at room temperature. A red precipitate (selenium) gradually appeared. After 10 min, the solution was worked up as in the case of **1***a*. Preparative tlc (50% $C_6H_6$ – hexane) afforded 77 mg of an unseparated mixture of **2***e* and **8**, whose respective yields of 39% and 47% were determined from the integrated intensities of their nmr signals.

trans-*3,3′-Bis(2-oxazolidinonyl)diazene* (**2**f)

*Under standard conditions*

3-Amino-2-oxazolidinone sulfate (**1***f*) (100 mg, 0.50 mmol) was oxidized with **3** (95 mg, 0.50 mmol) as in the case of **1***a*. The reaction mixture was allowed to warm to room temperature and an insoluble white solid was filtered to afford 48 mg (96%) of **2***f*; mp 295–300°C dec. (lit. (4) mp 298–299°C); identified by its uv and ir spectra (4).

*With $SeO_2$ as oxidant*

When $SeO_2$ was employed instead of **3** in the above procedure, the filtered solid consisted of starting material **1***f* contaminated by a trace of tetrazene **2***f* (detected by tlc) even after a reaction time of 43 h at room temperature.

trans-N,N′-*Bis(phthalimido)diazene* (**2**g)

*N*-Aminophthalimide (**1***g*) (162 mg, 1.00 mmol), seleninic acid **3** (189 mg, 1.00 mmol), and sulfuric acid (98 mg, 1.00 mmol) were stirred 45 min in 3 mL of MeOH at room temperature. An insoluble white solid was then filtered to afford 137 mg (86%) of **2***g*; mp 295°C dec. (lit. (8) mp 294–299°C dec.); identified by its ir and mass spectra (8). When the experiment was performed without sulfuric acid, only unreacted **1***g* was recovered.

*Trapping of* N-*phthalimidonitrene from* **1**g *and* **3** *with DMSO*

Hydrazine **1***g* (81 mg, 0.50 mmol) and seleninic acid **3** (95 mg, 0.50 mmol) were stirred in 1 mL of dry DMSO at room temperature. After 10 min, DMSO was removed from the yellow solution *in vacuo* and the residue was separated by preparative tlc (10% MeOH – $CHCl_3$) to provide, in decreasing order of mobility, 74 mg of diphenyl diselenide, 11 mg (15%) of phthalimide, identical to an authentic sample (mp, tlc, ir), and 21 mg (18%) of *S,S*-dimethyl-*N*-phthalimidosulfoximine (**11**); mp 208–210°C (lit. (18) mp 208–210°C); nmr (60 MHz) δ: 7.75 (m, 4H, aromatic), 3.28 (s, 6H, $CH_3$), with ir and mass spectra as reported in the literature (18). More polar components were poorly separated and were not further investigated.

*Oxidation of* N-*amino-2,2,6,6-tetramethylpiperidine* (**1**h) *with* **3**

Hydrazine **1***h* (70 mg, 0.45 mmol) and seleninic acid **3** (85 mg, 0.45 mmol) were added to 5 mL of MeOH at −70°C. No reaction was evident and the mixture was slowly permitted to warm to room temperature. At ca. −5°C, a yellow colour appeared and gas evolution commenced, becoming increasingly vigorous as warming continued. No significant amount of tetrazene **2***h* could be isolated from the mixture. When the reaction was repeated in $CDCl_3$ solution at room temperature, copious gas evolution occurred and the nmr spectrum of the remaining solution revealed a complex mixture of products.

*Oxidation of* N-*methyl*-N-*phenylhydrazine* (**1**i) *and* N,N-*diphenylhydrazine* (**1**j) *with* **3**

Hydrazine **1***i* (122 mg, 1.00 mmol) was oxidized with **3** (189 mg, 1.00 mmol) under the standard conditions described for **1***a*. Separation by preparative tlc (20% EtOAc – hexane) afforded 75 mg (29%) of *N*-methyl-*p*-phenylselenoaniline (**16**) as an oil, identical to an authentic sample (*vide infra*) in all respects, as well as a large number of unidentified products. The similar oxidation of **1***j* produced an extremely complex mixture containing at least ten components (tlc), which was not further investigated.

N-*Methyl*-p-*phenylselenoaniline* (**16**)

Freshly redistilled *N*-methylaniline (107 mg, 1.00 mmol) and benzeneselenenyl chloride (191.5 mg, 1.00 mmol) were stirred 3 min in 3 mL of MeOH at room temperature. The reaction mixture was evaporated *in vacuo* and separated as in the preceding procedure to provide 73 mg (28%) of **16**; ir (film): 3425, 1595, 1577, 1500, 1475, 1435, 1318, 1290, 1260, 1180, 1019, 810, 730, 685 $cm^{-1}$; nmr (200 MHz) δ: 7.44 (d, $J$ = 8.5 Hz, 2H, $C_6H_4$), 7.35–7.10 (m, 5H, Ph), 6.55 (d, $J$ = 8.5 Hz, 2H, $C_6H_4$), 3.86 (br s, exchanged, 1H, NH), 2.84 (s, 3H, $CH_3$); mass spectrum, *m/e* 263 ($M^+$, $^{80}Se$), 261 ($M^+$, $^{78}Se$). *Anal.* calcd. for $C_{13}H_{13}NSe$: C 59.54, H 5.01, N 5.34; found: C 59.51, H 5.02, N 5.36.

*Oxidation of* N-*benzyl*-N-p-*toluenesulfonylhydrazine* (**1**k) *with* **3**

*In $CHCl_3$*

Hydrazine **1***k* (138 mg, 0.50 mmol) and seleninic acid **3** (95 mg, 0.50 mmol) were stirred 10 min in 5 mL of $CHCl_3$ at room temperature. A vigorous reaction with gas evolution was observed. The reaction mixture was concentrated *in vacuo* and separated by preparative tlc (20% EtOAc – hexane) to afford three main components. The top band provided 30 mg of a yellow oil consisting of diphenyl diselenide and benzyl phenyl selenide in a molar ratio of 57:43 (yield of selenide: 9%), as determined by integration of the nmr spectrum of the mixture. The identities of these two products was confirmed by gc – mass spectral analysis. The second band was further separated by preparative tlc ($CH_2Cl_2$) to give 46 mg (30%) of selenosulfonate **19**, identical to an authentic sample (12) (mp, ir, nmr), and 31 mg (25%) of benzyl *p*-toluenesulfinate (**18**) obtained as an oil (lit. (41) mp 22–24°C); ir (film): 1596, 1499, 1455, 1132 $cm^{-1}$; nmr spectrum as reported in the literature (42). The bottom component afforded 47 mg (38%) of sulfone **17**, mp 140–144°C (lit. (43) mp 144–145°C), identified by its ir and nmr spectra (44).

*In MeOH*

The above reaction was repeated in 5 mL of MeOH. The solution slowly turned clear and yellow. An internal standard (*p*-xylene) was added after 45 min at room temperature and gc analysis revealed the presence of 43 mg (70%) of benzyl methyl ether, further identified by gc – mass spectrometry. The mixture was then separated by preparative tlc ($CH_2Cl_2$) to afford 16 mg of diphenyl diselenide containing a trace of benzyl phenyl selenide, 111 mg (71%) of selenosulfonate **19**, and 25 mg (20%) of sulfinate ester **18**.

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