Selenium–nitrogen bond formation by ring expansion: synthesis of the 1,4,2-diselenazine ring system, fragmentation to a 1,2-diselenete and reactions to yield 1,4-diselenin derivatives

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1,3-Diselenolium cation salt 1 reacts with ammonia and iodine to afford the novel 1,4,2-diselenazine system 6 (40% yield) which fragments to yield dimethylcyanamide 8 and diselenin 9, presumably *via* intermediate 1,2-diselenete 7, which is trapped with dimethyl acetylenedicarboxylate to yield the cycloadduct 10.

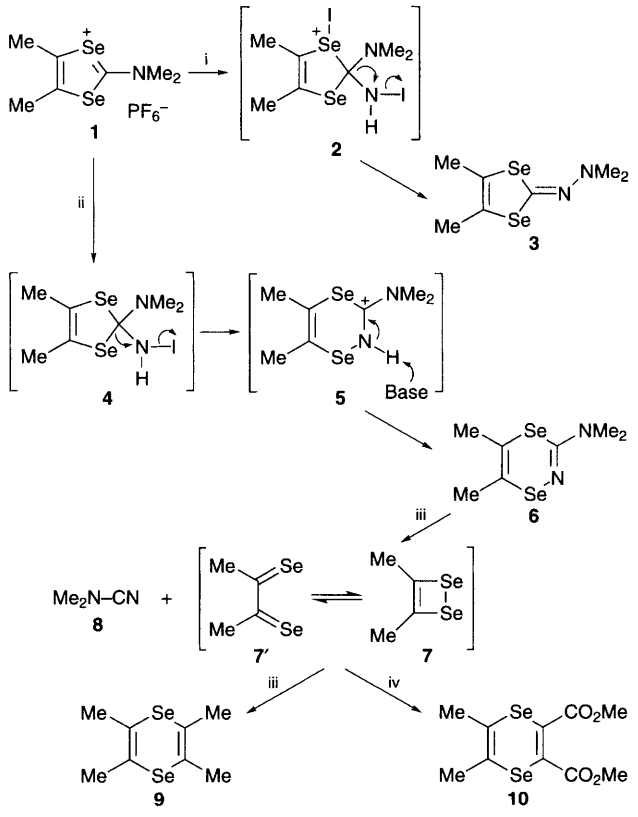
The chemistry of compounds containing selenium–nitrogen bonds[1] has received considerably less attention than their sulfur–nitrogen analogues. This is primarily due to the limited number of methods that are available for synthesising the selenium–nitrogen linkage, and to its instability in many compounds. Notable exceptions are five-membered C–N–Se heterocycles which are stabilised by 6π electron heteroaromaticity, either as the neutral species, *e.g.* 1,2,5-selenadiazoles,[1a] or as the cation, for which recent examples are 1,2,3,5-diselenadiazolium,[2] 1,2,4-diselenazolium[3] and 1,3,2-diselenazolium.[4] Six-membered C–N–Se heterocycles are rare, but a few examples are known.[5]

It has recently been established that 1,4,2-dithiazines are formed by ring expansion of 1,3-dithiolium cations upon reaction with a mixture of iodine and ammonia (presumably generating an NH_3–NI_3 complex *in situ*) at room temperature.[6] We recognised the potential of this methodology as a new approach to six-membered heterocycles containing a selenium–nitrogen bond. We now report that starting from the readily-available 1,3-diselenolium cation salt **1**,[7] a modification of this method has provided the first synthesis of the 1,4,2-diselenazine ring system **6**, and we describe fragmentation reactions of **6** which afford, ultimately, 1,4-diselenin derivatives **9** and **10**.

Dropwise addition of aqueous ammonia solution to a mixture of cation salt **1** and an excess of iodine in acetonitrile at room temperature, led to the formation of the stable hydrazone derivative **3**† (90% yield) resulting from nitrogen insertion into the exocyclic carbon–nitrogen bond in **1**, with none of the ring-expanded product **6** being detected in the reaction mixture. However, when the order of addition of iodine and ammonia was reversed (*i.e.* iodine was added to a mixture of **1** and ammonia) the major product was the 1,4,2-diselenazine derivative **6** (*ca.* 40%) alongside the hydrazone derivative **3** (*ca.* 20%). When ammonia and iodine were added simultaneously to an acetonitrile solution of **1**, compound **6** was not observed: the product mixture contained hydrazone **3** (16%), dimethylcyanamide **8** (5%) and 2,3,5,6-tetramethyl-1,4-diselenin **9** (5%). It is clear, therefore, that, unlike the analogous reactions of 1,3-dithiolium salts,[6] the products obtained from reaction of **1** with the iodine–ammonia system are critically dependent upon the reaction conditions.

A possible mechanism for the formation of these products is shown in Scheme 1. The key step in the preparation of 1,4,2-diselenazine derivative **6**, is formation of the selenium–nitrogen linkage, which most likely occurs by nucleophilic displacement of iodide from some form of adduct, *e.g.* intermediate **4**, derived from the NH_3–I_2 reagent, initially to yield cation **5**, which is then deprotonated to afford the product **6**. Hydrazone **3** could be formed *via* intermediate **2**, where the nucleophilicity of the selenium atom has been reduced by a prior reaction of the 1,3-diselenole ring with iodine, for which there is precedent with inorganic selenium-containing heterocycles.[8] The formation of **8** and **9** is consistent with fragmentation of the 1,4,2-diselenazine ring **6** to form the nitrile **8**, and the unstable 1,2-diselenete **7** (which is probably of lower energy than the 1,2-diselone tautomer **7′**).[4] Compound **9** could be derived from **7** either by loss of one selenium atom followed by dimerisation,[9] or, less likely, by initial dimerisation of **7** to yield the eight-membered ring,[4] which could then lose two selenium atoms to afford **9**.

Although compound **6** is an unsaturated 8π-electron heterocyclic system, when isolated from the reaction mixture, it is stable in chloroform solution at −5 °C for several weeks (^{1}H NMR evidence). Upon storage at 20 °C, compound **6** decomposed over a few days to yield a complex mixture of uncharacterised products (*cf.* the analogous 1,4,2-dithiazine system is stable for several months under these conditions).‡ It is noteworthy that in the mass spectrum of **6**,† there is a major fragment corresponding to the 1,2-selenazole derivative§



Scheme 1 *Reagents and conditions*: i, I_2 (excess) then NH_4OH (aq.) (excess), MeCN, 20 °C; ii, NH_4OH (aq.) (excess) then I_2 (excess), MeCN, 20 °C; iii, NH_4OH (aq.) (excess) and I_2 (excess) added simultaneously, MeCN, 20 °C; iv, dimethyl acetylenedicarboxylate (excess), 20 °C

formed by loss of one selenium atom, whereas this product was not detected from the decomposition of **6** in solution.

Addition of dimethyl acetylenedicarboxylate to a solution of **6** in acetonitrile at −5 °C resulted in no reaction; when the temperature of this mixture was raised to 20 °C, the novel 1,4-diselenin derivative **10** was isolated in 10% yield, after chromatographic separation from the unidentified decomposition products of **6**. The isolation of **10**, albeit in low yield, is very significant as it provides, to the best of our knowledge, the first evidence for the trapping of a 1,2-diselenete (or its 1,2-diselone tautomer) in a Diels–Alder reaction. The analogous trapping of 1,2-dithiones to yield 1,4-dithiins is known.[10]

We thank the EPSRC for funding this work. M. R. B. thanks the University of Durham for the award of a Sir Derman Christopherson Fellowship.

Footnotes

† All new compounds gave satisfactory ^{1}H NMR spectra and mass spectrometric data. **3**: ^{1}H NMR δ ($CDCl_3$) 2.30 (6 H, s) and 3.20 (6 H, s). *m/z* found: 283.9344, $C_7H_{12}N_2Se_2$ requires 283.9331; **6**: ^{1}H NMR δ ($CDCl_3$) 2.31 (3 H, s), 2.32 (3 H, s) and 3.32 (6 H, s). *m/z* (CI) 285 [M^+ + 1 (^{80}Se)] and 204.0162 (M^+ − Se), $C_7H_{12}N_2Se$ requires 204.0165; **9**: ^{1}H NMR δ ($CDCl_3$) 2.25 (12 H, s). *m/z* found: 267.9269, $C_8H_{12}Se_2$ requires 267.9286; **10**: ^{1}H NMR δ ($CDCl_3$) 3.85 (6 H, s) and 2.20 (6 H, s). *m/z* found: 355.9071, $C_{10}H_{12}O_4Se_2$ requires 355.9065.

‡ Addition of a mixture of ammonia and iodine to a solution of **6** in $CHCl_3$ at room temperature resulted in the very rapid decomposition of **6**.

§ We assign the 1,2-selenazole structure to this fragment, rather than the 1,3-selenazole isomer, by analogy with the corresponding thermal decomposition of 1,4,2-dithiazines observed in solution studies.[6b] It is noteworthy that this fragment was not observed in the mass spectrum of hydrazone **3**, confirming that it is derived from compound **6**.

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Received, 29th July 1996; Com. 6/05265G