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1,2,3-Trithiole, 1,2,3-Triselenole, and 1,2,5-Thiadiselenole. Novel Ring Systems Derived from Sterically Protected 1,2,3-Selenadiazole

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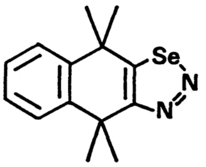
Thermal reactions of sterically protected 1,2,3-selenadiazole with elemental sulfur and selenium resulted in a formation of very stable 1,2,3-trithiole and 1,2,3-triselenole. Novel 1,2,5-thiadiselenole was also obtained by the sulfurization of the 1,2,3-triselenole.

The chemistry of cyclic polysulfides has attracted much attention from the viewpoints of not only their unique physical and chemical properties but also their biological activities,[1] and some 1,2,3,4,5-pentathiepins and 1,2,3-trithioles have been synthesized and characterized.[2] However, most examples of them have been restricted to the aromatic and heteroaromatic fused systems probably due to their much less stability than the linear polysulfides, and the intrinsic nature of these interesting heterocycles without the influence of fused aromatic ring still remains to be studied as an important problem. Furthermore, there have been no reports on their selenium analogues such as 1,2,3,4,5-pentaselenepins and 1,2,3-triselenoles so far as we know.[3]



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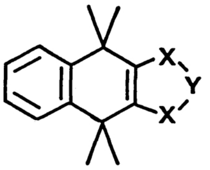
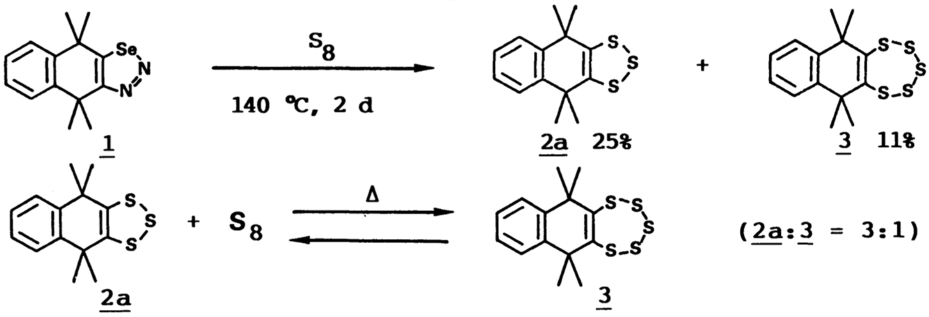


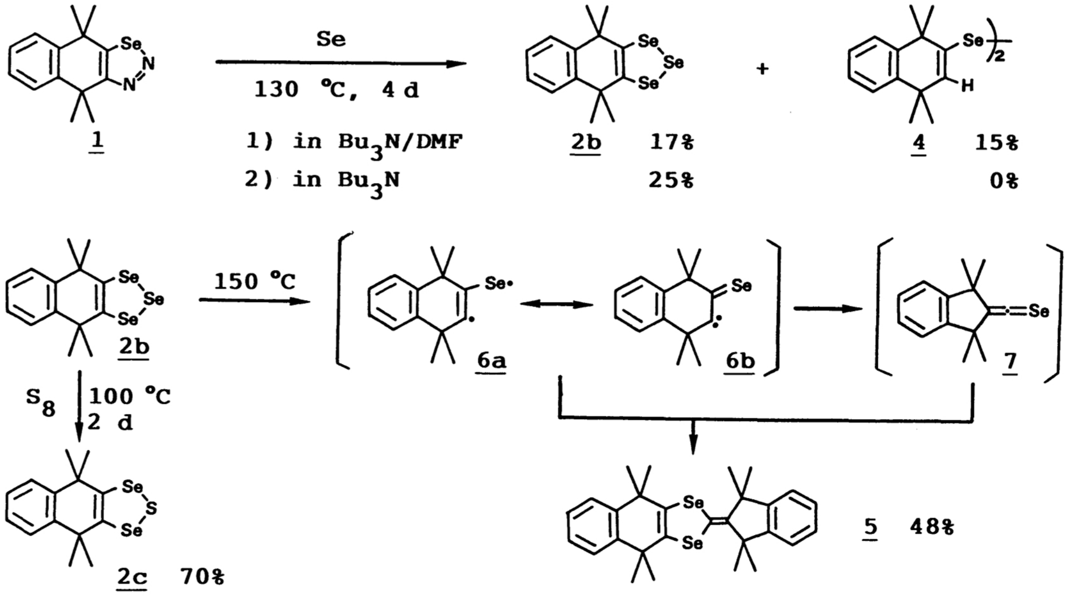
2a (X = Y = S)
2b (X = Y = Se)
2c (X = Se, Y = S)

We present here a novel formation of very stable 1,2,3-trithiole(**2a**), 1,2,3-triselenole(**2b**), and 1,2,5-thiadiselenole(**2c**) ring systems using a new type of sterically protected 1,2,3-selenadiazole (**1**) as a starting material, whose crowded fused ring is expected to be not so strained but bulky enough to stabilize the labile cyclic polysulfides and cyclic polyselenides.[4]

When the 1,2,3-selenadiazole(**1**)(318 mg, 1.1 mmol) was treated with excess of molten sulfur (1.0 g, 31 mmol as S_8) at 140 °C for two days, the 1,2,3-trithiole(**2a**)(75 mg, 25%) and the 1,2,3,4,5-pentathiepin(**3**)(50 mg, 11%) were isolated in a pure and stable crystalline form after column chromatography (SiO_2, hexane) followed by high pressure liquid chromatography purification. The remarkable stability of the sterically protected 1,2,3-trithiole(**2a**) here obtained is worthy of note in comparison with that of aromatic fused ones.[2a,b] Of another particular note with regards to the cyclic polysulfides **2a** and **3** is that the thermolysis of **3** at 140 °C in o-dichlorobenzene readily reached to an equilibrated mixture of **2a**, **3**, and S_8 (**2a**/**3** ratio was 3:1 as judged by ^{1}H-NMR spectroscopy), which was alternatively generated by heating the o-dichlorobenzene solution of **2a** mixed with S_8 at the same temperature. The equilibrium ratio certainly shows the relative stability of **2a** and should be compared to the Chenard's equilibrated cyclic polysulfides the ratio of which has been reported as almost 1:1.[2b)]



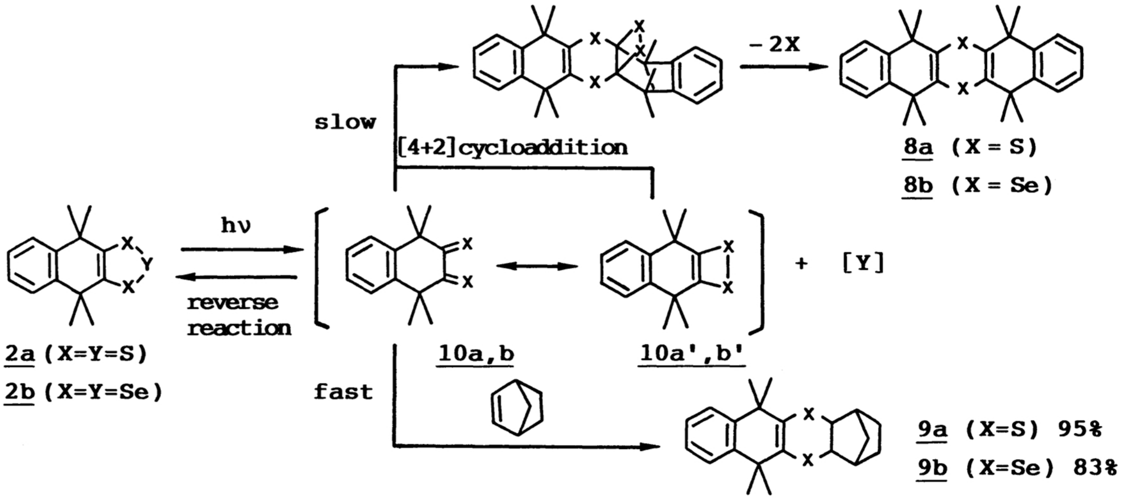
Although **1** was quite inert to elemental selenium alone in a polar solvent such as N,N-dimethylformamide(DMF) below its decomposition temperature (ca. 140 °C), when this reaction was performed at 130 °C in a mixed solvent of tributylamine and DMF (1:1) for four days the expected 1,2,3-triselenole(**2b**) was obtained as brownish orange crystals (mp 140-140.5 °C) in 17% yield together with the diselenide derivative(**4**, 15%). Furthermore, it was found that the use of tributylamine as a single solvent entirely suppressed the diselenide formation and resulted in an improvement of the yield of **2b** up to 25%.



2b was very stable even at its melting point and gradually thermolyzed in o-dichlorobenzene at 150 °C to give the 1,3-diselenole derivative(**5**)[5)] in 48% yield probably via the coupling of the initially formed deselenated intermediates(**6a** and **6b**) with the unstable selenoketene(**7**) which was the rearranged product from **6b**. When **2b** was treated with elemental sulfur in o-dichlorobenzene at 100 °C for two days, the corresponding 1,2,5-thiadiselenole(**2c**) was obtained as orange crystals(mp 128-129 °C) in 70% yield.

The structure of **2a**, **2b**, **2c**, and **3** thus obtained was confirmed by ^{1}H-NMR, ^{13}C-NMR, UV, and MS spectra and elemental analysis.$^{6)}$ **2b** and **2c** are the first examples of 1,2,3-triselenole and 1,2,5-thiadiselenole ring systems and the isolation of these new types of heterocycles in a stable crystalline form is one of the successful results of the effective steric protection of the fused tetramethyl-substituted dihydronaphthalene ring, however, the subtle steric requirement and ring strain of this fused system seem to disfavor the formation of other expected but labile cyclic polyselenides such as 1,2,3,4-tetraselenin or 1,2,3,4,5-pentaselenepin skeletons.

The photochemical reactions of **2a**, **2b**, and **3** were also examined. With the light of λ = 365 nm **3** was smoothly desulfurized into **2a** quantitatively and **2a** and **2b** were photolyzed very slowly (ca. 20% of substrate was consumed after the irradiation for ten days) to give the corresponding 1,4-dithiin(**8a**) and 1,4-diselenin(**8b**), respectively. On the contrary, in the presence of reactive olefin such as norbornene the photolysis of **2a** and **2b** readily proceeded to afford the cycloadducts **9a** and **9b** in 95 and 83% yields, respectively.



These results suggest the possible reverse reaction of the initially formed 1,2-dithione(**10a**) or 1,2-diselone(**10b**) with the once released sulfur or selenium atom, which may compete with the cycloaddition reaction of **10a** or **10b** to norbornene. In the absence of such appropriate trapping reagents the intermediary **10a** or **10b** slowly undergoes [4+2]cycloaddition with its tautomeric 1,2-dithiete(**10a'**) or 1,2-diselenete(**10b'**) form followed by the extrusion of sulfur or selenium leading to the formation of **8a** or **8b**.$^{7)}$

References

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Patterson, J. Org. Chem., 48, 112 (1983) and references cited in these reports.

2) a) B. L. Chenard and T. J. Miller, J. Org. Chem., 49, 1221 (1984); b) B. L. Chenard, R. L. Harlow, A. L. Johnson, and S. A. Vladuchick, J. Am. Chem. Soc., 107, 3871 (1985); c) F. Fehér and M. Langer, Tetrahedron Lett., 1971, 2125; d) F. Fehér and B. Engelen, Z. Anorg. Allg. Chem., 452, 37 (1979); e) F. Fehér, M. Langer, and R. Volkert, Z. Naturforsch., B, 27, 1006 (1972); f) R. Sato, S. Saito, H. Chiba, T. Goto, and M. Saito, Chem. Lett., 1986, 349 and references cited therein.

3) As an example of cyclic 1,2,3-triselenide, only the parent 1,2,3-triselenolane has been reported by M. P. Cava et al.; J. Org. Chem., 45, 2632 (1980).

4) We have recently described a facile formation of 1,2,3,4-tetrathiin and 1,2,3,4,5-pentathiepin derivatives along with 1,2,3,4,5-tetrathiaselenepin derivative by the sulfurization of sterically protected bicyclic 1,2,3-selenadiazole; W. Ando, Y. Kumamoto, and N. Tokitoh, Tetrahedron Lett.,28, 4833 (1987).

5) **5**: white crystals, mp 305 °C(sublimation), ^{1}H-NMR(CDCl$_3$) δ 1.58(s,6H), 1.66(s,6H), and 7.2-7.4(m,8H); ^{13}C-NMR(CDCl$_3$) δ 25.8(q), 33.9(q), 41.6(s), 50.7(s), 122.4(d), 125.9(d), 126.4(d), 127.1(d), 128.3(s), 138.5(s), 141.0(s), 147.5(s), and 149.8(s); MS m/z 528(M^+,50%) and 513(100); Found: m/z 528.0816 (Calcd for $C_{28}H_{32}Se_2$: M, 528.0832).

6) **2a**: orange crystals, mp 139.5-140 °C, ^{1}H-NMR(CDCl$_3$) δ 1.56(s,12H) and 7.2-7.4(m,4H); ^{13}C-NMR(CDCl$_3$) δ 31.4(q), 40.7((s), 125.8(d), 126.7(d), 140.5(s), and 141.7(s); MS m/z 280(M^+,66%), 233(33), 201(100), and 186(29); Found:C,59.73; H,5.77% (Calcd for $C_{14}H_{16}S_3$ C,59.95; H,5.75%); UV(hexane) λ_{max} 378nm (ε110). **2b**: brownish orange crystals, mp 140-140.5 °C, ^{1}H-NMR(CDCl$_3$) δ 1.61(s,12H) and 7.1-7.4(m,4H); ^{13}C-NMR(CDCl$_3$) δ 32.4(q), 43.7(s), 126.1(d), 126.5(d), 140.4(s), and 145.2(s); MS m/z 424(M^+,19%), 344(16), 329(16), and 169(100); HRMS, Found:m/z 423.8725 (Calcd for $C_{14}H_{16}Se_3$: M,423.8727); UV(hexane) λ_{max} 320nm(ε320). **2c**: orange crystals, mp 128-129 °C, ^{1}H-NMR(CDCl$_3$)δ1.59(s,12H) and 7.15-7.40(m,4H); ^{13}C-NMR(CDCl$_3$) δ 32.5(q), 43.2(s), 126.0(d), 140.5(s), and 144.4(s); MS m/z 376(M^+,47%), 329(100), and 249(65); Found:C,45.12; H,4.36 (Calcd for $C_{14}H_{16}SSe_2$ C,44.92; H,4.30);UV(hexane) λ_{max} 317 nm(ε340) and 403 nm(140). **3**: yellow crystals, mp 159-160 °C, ^{1}H-NMR(CDCl$_3$) δ 1.46(s,6H), 1.74(s,6H), and 7.2-7.4(m,4H); ^{13}C-NMR(CDCl$_3$) δ 29.1(q), 32.0(q), 43.2(s), 126.6(d), 126.7(d), 139.6(s), and 154.7(s); MS m/z 344(M^+, 0.6%), 280(46), 201(100), and 169(86); Found:C,48.94; H,4.84% (Calcd for $C_{14}H_{16}S_5$ C,48.80; H,4.68%); UV(hexane) λ_{max} 287 nm (ε2200).

The other products described in this paper gave satisfactory spectral data and their composition was ascertained by elemental analysis and/or high resolution mass spectroscopy.

7) Cava et al. have already postulated similar mechanism for the 1,4-dithiin formation in the thermal reaction of 1,2-dithione; A. Orahovatz, M. I. Levinson, P. J. Carroll, M. V. Lakshmikantham, and M. P. Cava, J. Org. Chem., 50, 1550 (1985).

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