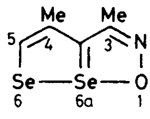
# Reaction of 3,4-Dimethyl-1-oxa-6,6a$\lambda^4$-diselena-2-azapentalene with Tetraphosphorus Decasulphide: A New Molecular Rearrangement. *X*-Ray Crystal Structures of 3,4-Dimethyl-1-oxa-6,6a$\lambda^4$-diselena-2-azapentalene, 2,4-Dimethyl-1-thia-6,6a$\lambda^4$-diselena-3-azapentalene, and 2,4-Dimethyl-1,6-dithia-6a$\lambda^4$-selena-3-azapentalene

**Christine Allen,[a] Jan C. A. Boeyens,[a] Alexander G. Briggs,[b] Louis Denner,[a] (the late) Anthony J. Markwell,[a] David H. Reid,*[a] and Beate G. Rose[a]**

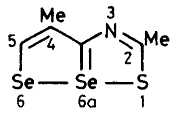
[a] *Department of Chemistry, University of the Witwatersrand, 1 Jan Smuts Avenue, Johannesburg 2001, South Africa*
[b] *Department of Chemistry, The Purdie Building, The University, St Andrews KY16 9ST, Scotland*

The title compound (**1**) reacts with tetraphosphorus decasulphide to give two molecular rearrangement products (**2**) and (**3**), together with compound (**4**); the structures of compounds (**1**)—(**3**) have been established by *X*-ray single crystal analyses.

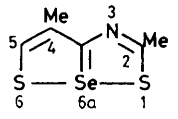
In the course of attempts to synthesise 1,6,6a$\lambda^4$-triheterapentalenes containing the N–S unit, we have carried out reactions of the oxadiselena-azapentalene (**1**)[1] with thiophosphoryl reagents in order to effect exchange of oxygen for sulphur, as in the well known C=O → C=S conversions. Using $P_4S_{10}$ in boiling benzene, we obtained three products† from compound (**1**). Two of these have the structures (**2**) and (**3**), established by *X*-ray single crystal structure determinations (Figures 1 and 2).‡ We have not yet obtained crystals of the third product suitable for an *X*-ray crystal structure determination, but analytical, $^1H$ n.m.r., and mass spectral data indicate that it has structure (**4**). The mass spectral patterns of compounds (**1**) and (**4**) are very similar, and both compounds show strong $M^+ - 30$ peaks corresponding to the loss of NO from the molecular ion.



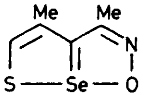
(**1**)



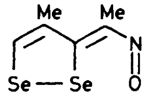
(**2**)



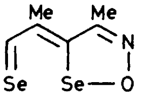
(**3**)



(**4**)



(**5**)



(**6**)

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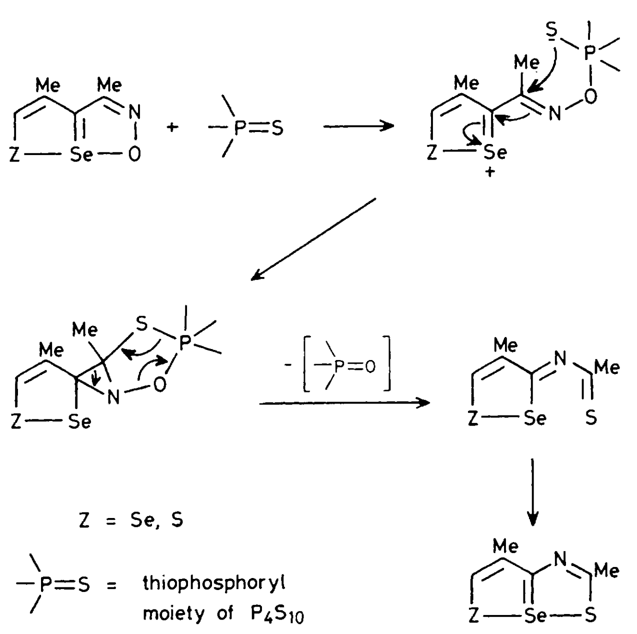
† Compound (**2**), red crystals, m.p. 103—105 °C; compound (**3**), orange crystals, m.p. 84—86.5 °C; compound (**4**), rust-red crystals, m.p. 117—118.5 °C. Satisfactory C, H, and N microanalyses were obtained for compounds (**2**)—(**4**). $^1H$ n.m.r. spectral data ($CDCl_3$, $J$ in Hz, $Me_4Si$ reference, 200 MHz): (**2**), $\delta$ 2.796 (3H, d, $J_{4\text{-Me},5}$ 0.66, 4-Me), 2.879 (3H, 2-Me), 10.373 (1H, q, $J_{5,4\text{-Me}}$ 0.66, 5-H); (**3**), $\delta$ 2.731 (3H, d, $J_{4\text{-Me},5}$ 0.74, 4-Me), 2.923 (3H, 2-Me), 9.437 (1H, q, $J_{5,4\text{-Me}}$ 0.74, 5-H); (**4**) $\delta$ 2.984 (3H, d, $J_{4\text{-Me},5}$ 0.73, 4-Me), 3.017 (3H, 3-Me), 9.479 (1H, q, $J_{5,4\text{-Me}}$ 0.73, 5-H). (**2**), *m/z* 284.8616 ($M^{+\cdot}$); (**3**), *m/z* 236.9194 ($M^{+\cdot}$); (**4**), *m/z* 220.9418 ($M^{+\cdot}$).

‡ *Crystal data:* compound (**1**), $C_6H_7NOSe_2$, $M$ = 267.05, monoclinic, space group $P2_1/n$, $a$ = 11.693 (3), $b$ = 9.592(2), $c$ = 14.694(2) Å, $\beta$ = 104.45 (2)° $U$ = 1595.9 Å$^3$, $Z$ = 8, $D_c$ = 2.223 g cm$^{-3}$, $F(000)$ = 1008, $\mu$ = 89.49 cm$^{-1}$; $R$ = 0.0387 for 1618 unique reflections, with $F_o \geqslant 4\sigma(F_o)$. Compound (**2**), $C_6H_7NSSe_2$, $M$ = 283.11, monoclinic, space group $C2/c$, $a$ = 16.933(4), $b$ = 4.132(8), $c$ = 24.911(7) Å, $\beta$ = 94.20(2)°, $U$ = 1738 Å$^3$, $Z$ = 8, $D_c$ = 2.163 g cm$^{-3}$, $F(000)$ = 1072, $\mu$ = 84.34 cm$^{-1}$; $R$ = 0.0377 for 1365 unique reflections, with $F_o \geqslant 4\sigma(F_o)$. Compound (**3**), $C_6H_7NS_2Se$, $M$ = 236.22, monoclinic, space group $P2_1/c$, $a$ = 8.112(1), $b$ = 4.029(3), $c$ = 25.965(6) Å, $\beta$ = 90.26(2)°, $U$ = 848.6 Å$^3$, $Z$ = 4, $D_c$ = 1.849 g cm$^{-3}$, $F(000)$ = 464, $\mu$ = 46.80 cm$^{-1}$; $R$ = 0.0416 for 1754 unique reflections, with $F_o \geqslant 4\sigma(F_o)$. Data were collected using an Enraf-Nonius CAD4F diffractometer with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The structures were solved by heavy atom methods and refined by full-matrix least-squares (unit weights) with anisotropic thermal parameters for all non-hydrogen atoms, and a common isotropic thermal parameter for the hydrogen atoms [except H(5) in compound (**1**) which was allowed to refine freely). Lorentz-polarisation and empirical absorption corrections were applied to all data. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

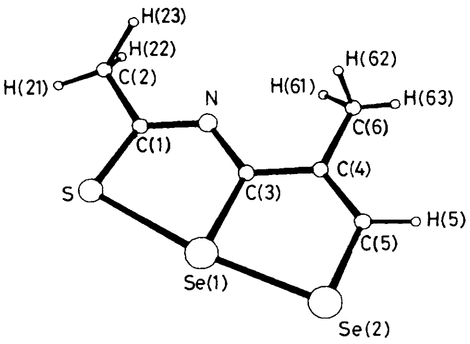


**Figure 1.** The molecular structure and atomic numbering scheme for compound (**2**). Selected parameters are: Se(1)–Se(2) 2.473(1), Se(1)–S 2.507(2), Se(1)–C(3) 1.906(6), Se(2)–C(5) 1.830(8), S–C(1) 1.681(8), N–C(1) 1.302(9), N–C(3) 1.350(9), C(3)–C(4) 1.402(10), C(4)–C(5) 1.367(11) Å; Se(2)–Se(1)–S 171.3(1), Se(2)–Se(1)–C(3) 88.7(2), S–Se(1)–C(3) 82.7(2), Se(1)–Se(2)–C(5) 89.3(3), C(1)–N–C(3) 121.0(6)°.

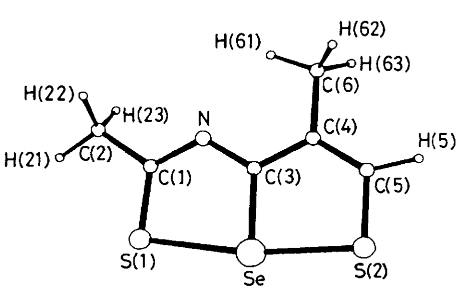


**Figure 2.** The molecular structure and atomic numbering scheme for compound (**3**). Selected parameters are: Se–S(1) 2.467(2), Se–S(2) 2.372(2), Se–C(3) 1.899(4), S(1)–C(1) 1.689(5), S(2)–C(5) 1.687(6), N–C(1) 1.310(6), N–C(3) 1.340(5), C(3)–C(4) 1.399(6), C(4)–C(5) 1.360(7) Å; S(1)–Se–S(2) 170.0(1), S(1)–Se–C(3) 83.3(1), S(2)–Se–C(3) 86.7(1), Se–S(1)–C(1) 91.6(2), Se–S(2)–C(5) 93.7(2), C(1)–N–C(3) 120.5(4).

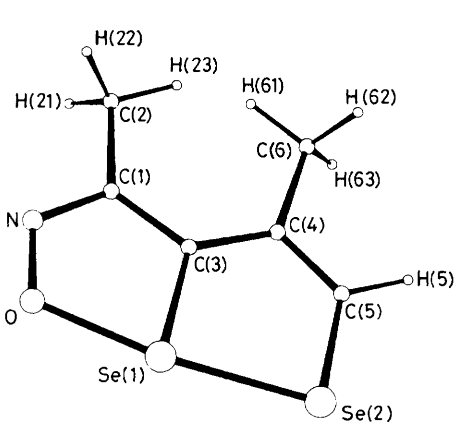


**Figure 3.** The molecular structure and atomic numbering scheme for compound (**1**). Selected parameters are (the values given are the averages of those of the two molecules of the asymmetric unit): Se(1)–Se(2) 2.444(2), Se(1)–O 2.043(8), Se(1)–C(3) 1.868(10), Se(2)–C(5) 1.821(13), O–N 1.318(12), N–C(1) 1.307(14), C(1)–C(3) 1.442(14), C(3)–C(4) 1.391(14), C(4)–C(5) 1.39(2) Å; Se(2)–Se(1)–O 171.0(2), Se(2)–Se(1)–C(3) 89.0(3), O–Se(1)–C(3) 82.9(4), Se(1)–O–N 112.2(6)°.

Formation of compounds (**2**) and (**3**) from (**1**) involves a new type of molecular rearrangement. We propose that the transformation (**1**) → (**2**) occurs by the mechanism in Scheme 1 (Z = Se). Compound (**4**) also reacted with $P_4S_{10}$ to give (**3**), whereas (**2**) did not. This suggests that compound (**3**) is formed *via* the seqence (**1**) → (**4**) → (**3**) rather than (**1**) → (**2**) → (**3**), with the rearrangement of Scheme 1 (Z = S) giving (**3**) from (**4**). The heterapentalene (**1**) is a masked form of both the nitroso compound (**5**) and the selenoaldehyde (**6**). Its potential nitroso reactivity is seen in the rearrangement process, and its latent selenocarbonyl reactivity is utilised in the transformation of compound (**1**) into (**4**). Compound (**4**) was the major product from the reaction of (**1**) with Lawesson's reagent,§ with only traces of (**2**) and (**3**) being formed.

We have also established the structure of the starting compound (**1**) by an *X*-ray single crystal structure determination (Figure 3).‡

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## References

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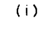
§ Lawesson's reagent has structure (i): B. S. Pedersen, S. Scheibye, N. H. Nilsson, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 223. For a review of thionation reactions with Lawesson's reagents, see M. P. Cava and M. I. Levinson, *Tetrahedron*, 1985, **41**, 5061.



(i)