# Isolation and Characterization of Selenoketens

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*Summary* Selenoketens, formed by pyrolysis of 4-alkyl-1,2,3-selenadiazoles in the vapour phase, may be isolated at −196 °C as highly coloured deposits and undergo characteristic chemical reactions.

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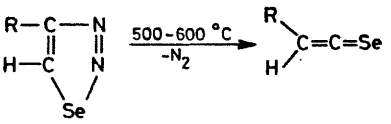
1,2,3-SELENADIAZOLES are reported to decompose to form acetylenes[1a] when heated in condensed phase, except for cycloalkenoselenadiazoles which also give 1,4-diselenines.[1b] However, it has recently been unambiguously demonstrated that pyrolysis of selenadiazole in the vapour phase gives selenoketen as identified by its microwave spectrum.[2] We now report that formation of selenoketens appears to be a general reaction when 4-alkyl-1,2,3-selenadiazoles are pyrolysed in the vapour phase (100—10 mTorr) at 500—600 °C [equation (1)].

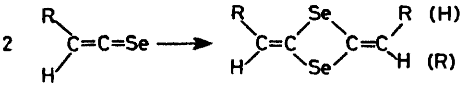


(1)

(1) (2)

a; R = H
b; R = Me
c; R = Bu$^t$

The selenoketens investigated have been trapped as highly coloured deposits at −196 °C. Compound (**2a**) is purple while (**2b**) and (**2c**) are blue. They are extremely labile with respect to thermal dimerization in the condensed phase [equation (2)]. The process, either spontaneous or provoked by slight heating, is evidenced by an abrupt change to the pale yellow colour of the dimers. Selenoketens (**2a**) and (**2c**) are characterized by their i.r. spectra at −196 °C on a KBr disc featuring strong absorptions at 1695 and 1700 cm$^{-1}$, respectively, which we assigned to the C=C=Se stretching vibrations.[3] In the case of (**2b**), the dimerization was too fast to permit the i.r. spectrum to be recorded and the presence of (**2b**) after pyrolysis of (**1b**) is evidenced only by the quickly fading colour and the appearance of the dimer (**3b**).

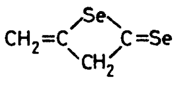


(2)

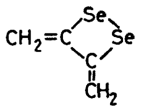
(2) (3)

a; R = H
b; R = Me
c; R = Bu$^t$

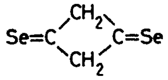
The dimers (**3a**—**c**) show satisfactory elemental analyses and mass spectra, the latter with the expected isotopic clusters due to two selenium atoms.[4] The structure assignment of the dimers is based on the $^1$H n.m.r. data:



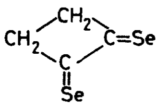
(**4a**)



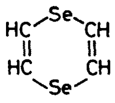
(**5a**)



(**6a**)



(**7a**)



(**8a**)

δ ($CDCl_3$, $Me_4Si$) (**3a**), oil, 6·37 (s, $CH_2$); (**3b**), semisolid, 6·47, 6·36 (q, CH, intensity ratio *ca.* 1 : 4 corresponding to the occurrence of a *cis–trans* mixture), and 1·84 (d, Me); (**3c**), m.p. 93—95 °C, 6·53 (s, CH) and 1·23 (s, Me). Alternative structures are ruled out because (**4a**) and most probably also (**5a**) would not display singlet $^1$H n.m.r. absorptions, (**6a**) and (**7a**) are expected to be highly coloured[5] in contrast to the pale yellow appearance, and the formation of (**8a**) would imply hydrogen migration, a process which is not very likely to occur at −196 °C.

Trapping of the pyrolysate from (**1a**) at −80 °C led to a polymer $(H_2C{=}C{=}Se)_n$, obtained as a brownish film insoluble in a variety of common organic solvents. Its constitution and the order of *n* is unknown so far.

When vapours of the selenoketen (**2a**) are mixed with vapours of dimethylamine immediately after generation, the expected formation of *NN*-dimethylselenoacetamide (m.p. 85—86 °C) takes place [equation (3)]. The product was

$$CH_2{=}C{=}Se + NHMe_2 \rightarrow Me{-}C({:}Se){-}NMe_2 \qquad (3)$$

identified by elemental analysis as well as by comparison with an authentic material[6] (superimposable i.r. spectra and lack of m.p. depression on admixture).

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[1] (a) I. Lalezari, A. Shafiee, and M. Yalpani, *Angew. Chem.*, 1970, **82**, 484; *J. Org. Chem.*, 1971, **36**, 2836; I. Lalezari, A. Shafiee, and H. Golgolab, *J. Heterocyclic Chem.*, 1973, **10**, 655; I. Lalezari, A. Shafiee, F. Rabet, and M. Yalpani, *ibid.*, p. 953; H. Meier and I. Menzel, *Tetrahedron Letters*, 1972, 445; H. Meier, S. Schniepp, and W. Combrink, *Chem.-Ztg.*, 1975, **99**, 461; (b) I. Lalezari, A. Shafiee, and M. Yalpani, *J. Heterocyclic Chem.*, 1972, **9**, 1411; H. Meier and E. Voigt, *Tetrahedron*, 1972, **28**, 187; H. Meier, M. Layer, and A. Zetzsche, *Chem.-Ztg.*, 1974, **98**, 460; H. Golgolab and I. Lalezari, *J. Heterocyclic Chem.*, 1975, **12**, 801; H. Petersen, H. Kolshorn, and H. Meier, *Angew. Chem.*, 1978, **90**, 483.

[2] B. Bak, O. J. Nielsen, H. Svanholt, and A. Holm, *Chem. Phys. Letters*, 1978, **53**, 374; 1978, **55**, 36.

[3] An intense band at 1695 cm$^{-1}$ observed when irradiating matrix isolated 1,2,3-selenadiazole at −265 °C was assigned to selenoketen; the corresponding mode in thioketen is observed at 1755 cm$^{-1}$: J. Laureni, A. Krantz, and R. A. Hajdu, *J. Amer. Chem. Soc.*, 1976, **98**, 7872.

[4] J. R. Andersen, H. Egsgaard, E. Larsen, K. Bechgaard, and E. M. Engler, *Org. Mass Spectrometry*, 1978, **13**, 121.

[5] Selenoketones are highly coloured compounds: T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J.C.S. Chem. Comm.*, 1975, 539. See also corresponding sulphur compounds; E. U. Elam and H. E. Davis, *J. Org. Chem.*, 1967, **32**, 1562.

[6] C. Collard-Charon and M. Renson, *Bull. Soc. chim. belges*, 1963, **72**, 304.