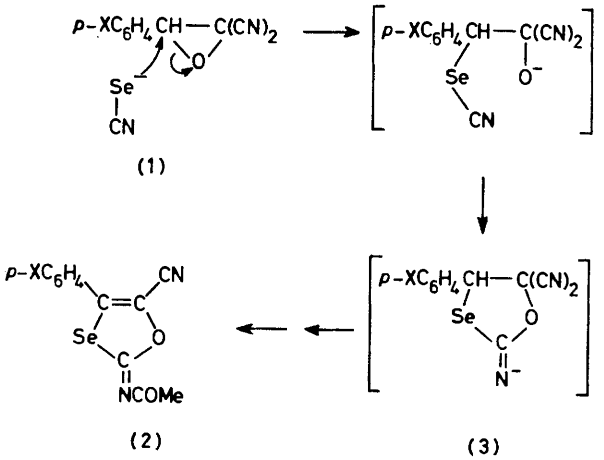
# Preparation of Derivatives of a New Heterocyclic System: 2-*N*-Acylimino-1,3-oxaselenoles

By Albert Robert* and Alenka Le Marechal

(*Groupe de Recherches de Chimie Structurale, E.R.A. 389, Université de Rennes, Avenue du Général Leclerc, Rennes, France*)

*Summary* Substituted 1,3-oxaselenoles are easily prepared by the reaction of *gem*-dicyano epoxides with potassium selenocyanate.

Starting from the readily accessible aryl dicyano-epoxides (**1**)[1] we have developed new synthetic routes to various heterocyclic compounds: 2-amino-$\Delta^4$-thiazolinones,[2] 4-hydroxythiazoles,[3] anhydro-4-hydroxythiazolium hydroxides,[4] and anhydro-4-hydroxy-1,3-selenazolium hydroxides.[5] We describe here the reaction of the epoxides (**1**) with potassium selenocyanate leading to the first compounds of the 1,3-oxaselenole series. The epoxides (**1**) in solution in acetic anhydride react at room temperature in a few minutes with an equimolecular amount of potassium selenocyanate. The 1,3-oxaselenoles (**2a**—**e**) obtained were characterized by their i.r., n.m.r., and high-resolution mass spectra. Typically, (**2a**) shows $\nu_{max}$ ($CCl_4$) 2229 (CN) and 1655 (CO) cm$^{-1}$; $\delta$ ($CDCl_3$) 2·44 (3H, s, Me), and 7·52 (5H, m, ArH).



(1) (2) (3)

| Product | X | M.p./°C | % Yield |
|---|---|---|---|
| (**2a**) | H | 137 | 40 |
| (**2b**) | Cl | 139 | 38 |
| (**2c**) | MeO | 173 | 56 |
| (**2d**) | $NO_2$ | 160 | 42 |

The strong absorptions observed about 2230 and 1655 cm$^{-1}$ are in agreement with the presence of a conjugated nitrile and carbonyl group, respectively. The only observed signals in the n.m.r. spectra are due to aryl and methyl protons. The selenium-containing fragments are easily recognized in the mass spectra from the typical distribution of natural isotopes.[6] In agreement with structure (**2**) $(ArCSe)^+$ is always observed and a metastable ion kinetic energy study has shown that $M^{+\cdot}$ gives $(ArCHCOCN)^+$ *via* $[ArCH(SeCN)COCN]^{+\cdot}$.

The mechanism of the reaction is not established. Nucleophilic ring opening of the epoxide by the selenocyanate anion would be a reasonable first step.[7] Formation of the intermediate (**3**) in $Ac_2O$ may then account for the formation of the 1,3-oxaselenole (**2**). When potassium thiocyanate was used instead of potassium selenocyanate, a similar reaction was observed, the corresponding substituted 1,3-oxathioles being obtained.

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[1] J. J. Pommeret and A. Robert, *Tetrahedron*, 1971, **27**, 2977.

[2] M. Ferrey, A. Robert, and A. Foucaud, *Compt. rend.*, 1973, **277C**, 1153.

[3] M. Ferrey, A. Robert, and A. Foucaud, *Synthesis*, 1976, 261.

[4] M. Baudy and A. Robert, *J.C.S. Chem. Comm.*, 1976, 23.

[5] A. Robert, M. Baudy, and A. Le Marechal, 'Sixth International Congress on Heterocyclic Chemistry,' Tehran, 1977.

[6] L. B. Agenäs, in 'Organic Selenium Compounds: Their Chemistry and Biology,' eds. D. L. Klayman and W. H. H. Günther, Wiley, New York, 1973, p. 963.

[7] M. Sander, *Chem. Rev.*, 1966, **66**, 297; J. M. Behan, R. A. W. Johnstone, and M. J. Wright, *J.C.S. Perkin I*, 1975, 1216.

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