Synthesis and Properties of Diaminocyclopropeneselone (Quasi-selenourea)

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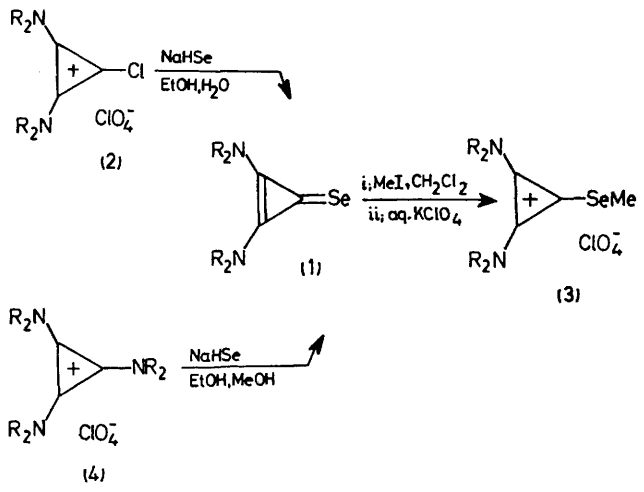
Summary Diaminocyclopropeneselone, a novel highly strained system is synthesized and its properties as quasi-selenourea are described.

OUR interest in quasi-urea and quasi-thiourea[1] has led us to investigate the synthesis and properties of quasi-selenourea, diaminocyclopropeneselone (**1**). When 1,2-bisdiisopropylamino-3-chlorocyclopropenium perchlorate (**2**, R = Pr^i) was treated with sodium hydrogen selenide, bisdiisopropylaminocyclopropeneselone (**1**, R = Pr^i) was obtained in almost quantitative yield (colourless crystals, m.p. 256°) No ring opening was observed to occur. This is the first synthesis of a cyclopropeneselone.



Its spectral data are in accord with the proposed structure. [i.r. (KBr) ν_{max} 1873, 1850 and 1492 cm^{-1}, spectrum resembling that of the corresponding thione in the fingerprint region; u.v. (MeCN) λ_{max} 280 (log ϵ, 4·22) and 234 nm (4·06); n.m.r. ($CDCl_3$) shows equivalent isopropyl groups, a doublet at τ 8·60 (J 6·6, 24H) and a septuplet at 6·16 (J 6·6 Hz, 4H); m.s., M^+ at m/e 316 and 314, but no peak at m/e 236 (M^+ — CSe)]. Diaminocyclopropeneselone was also synthesized by the reaction of the triaminocyclopropenium ion (**4**) with sodium hydrogen selenide. The selone is stable to air in crystalline form, and sublimed below its m.p. without decomposition. Reaction of (**1**, R = Pr^i) with methyl iodide in methylene chloride and successive treatment with aq. $KClO_4$ gave colourless crystals of 1,2-bis(diisopropylamino)-3-methylseleno-cyclopropenium perchlorate (**3**, R = Pr^i) in 53% yield, m.p. 180°. Its structure was confirmed by elemental analysis, i.r. (ν_{max} 1878, 1568 and 1095 cm^{-1}, u.v. [(MeCN) λ_{max} 275 (log ϵ, 3·63), 241 (sh), and 211 nm (4·21)] and n.m.r. [($CDCl_3$), τ 8·59 (24H, d, J 6·6), 7·44 (3H, s), and 6·02 (4H, sept., J 6·6 Hz].

The behaviour and structural properties of (**1**) are more like those of the corresponding thione than those of the corresponding cyclopropenone. The stability of (**1**) is ascribed to the strong π-conjugative interaction between the amino groups and the selenocarbonyl group through the cyclopropene ring. In view of similarity between (**1**) and selenourea in physical and chemical properties diaminocyclopropeneselone can be refered to as 'quasi-selenourea.'

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[1] Z. Yoshida, H. Konishi, Y. Tawara, and H. Ogoshi, *J. Amer. Chem. Soc.*, 1973, **95**, 3043; Z. Yoshida, H. Konishi, Y. Tawara, K. Nishikawa, and H. Ogoshi, *Tetrahedron Letters*, 1973, 2619.