Synthesis of Anhydro-2,3,5-triphenyl-4-hydroxyselenazolium Hydroxide, a Mesoionic Selenium Heterocycle

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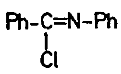
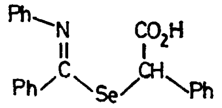
Summary The synthesis of anhydro-2,3,5-triphenyl-4-hydroxyselenazolium hydroxide (**4**) is reported which is the first example of a mesoionic selenium heterocycle.

Although a variety of mesoionic sulphur-containing heterocycles are known,[1] no analogous selenium compounds have been reported. We now report the synthesis and some properties of anhydro-2,3,5-triphenyl-4-hydroxyselenazolium hydroxide (**4**), the first mesoionic heterocycle containing an endocyclic selenium atom.

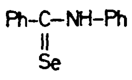
Treatment of *N*-phenylbenzimidoyl chloride (**1**) with sodium hydrogen selenide in EtOH—dioxan gave (89%) red-orange needles (benzene–hexane) of selenobenzanilide (**2**),† m.p. 113—115 °C; λ_{max} (EtOH) 247 (log ϵ 4·18), 458 nm (2·50); ν_{max} (KBr) 1625, 1500, 1400, and 1085 cm^{-1}. Reaction of (**2**) with α-bromophenylacetic acid and triethylamine in benzene gave the α-seleno acid (**3**), which was directly cyclized in the cold by 1 : 1 Et_3N–Ac_2O to give (88%) magenta needles (EtOH–light petroleum) of the selenazolone (**4**), m.p. 232 °C; λ_{max} (EtOH) 484 nm (log ϵ 4·00); ν_{max} (KBr) 1575 cm^{-1}. These data show a bathochromic shift in the visible maximum and the carbonyl absorption band of (**4**) compared with the values (453 nm and 1620 cm^{-1}, respectively) reported for the corresponding mesoionic thiazolone (**5**).[2]


$\mathrm{Ph{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}N{-}Ph}$

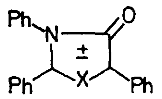
(1)



(3)

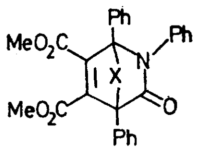

$\mathrm{Ph{-}\underset{\displaystyle Se}{\underset{\|}{C}}{-}NH{-}Ph}$

(2)



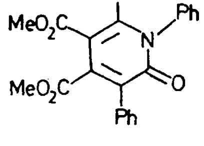
(4) X = Se

(5) X = S

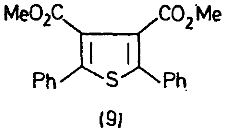


(6) X = Se

(7) X = S



(8)



(9)

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† Satisfactory elemental analyses and mass spectra were obtained for compounds (**2**) and (**4**).

The selenazolone (**4**) is surprisingly unreactive as a 1,3-dipole, the addition of dimethyl acetylenedicarboxylate (absence of light) requiring about one week in refluxing benzene. During this time, the primary adduct (**6**) undergoes spontaneous elimination of elemental selenium (*ca.* 90% recovery of amorphous Se) with the formation of the known[3] pyridone diester (**8**), m.p. 220–221 °C (65% after chromatography). In contrast, the corresponding dipolar addition reaction of the analogous thiazolone (**5**) is complete after refluxing overnight; the primary adduct (**7**) does not lose the sulphur bridge, but eliminates phenyl isocyanate with the exclusive formation (90% isolated) of the thiophen diester (**9**).[4]

We thank the National Science Foundation for support.

(*Received*, 12*th May* 1975; *Com.* 541.)

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[1] For some examples see: M. Ohta and H. Kato in 'Non-benzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, ch. 4, p. 117; H. Gotthardt and B. Christl, *Tetrahedron Letters*, 1968, 4743; W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15.

[2] Z. Takayanagi, H. Kato, and M. Ohta, *Bull. Chem. Soc. Japan*, 1967, **40**, 2930; M. Ohta, H. Chasho, C. Shin, and K. Ichimura, *J. Chem. Soc. Japan*, 1964, **85**, 440.

[3] K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, 1974, **39**, 3631.

[4] K. T. Potts, E. Houghton, and U. P. Singh, *J. Org. Chem.*, 1974, **39**, 3627.