

## A New Heterocycle: 2,7-Dihydro-1,4,5-selenadiazepine

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The synthesis of selenodiketones of types I and II has been previously reported (1,2), but there is no mention of the reaction of these diketones with hydrazine (only some phenylhydrazones were reported) (1).

In the course of our work concerning selenocompounds bis(selenoacetophenones) of type II had been prepared and it was of interest to us to examine the behaviour of these 1,5-diketo selenides with hydrazine.

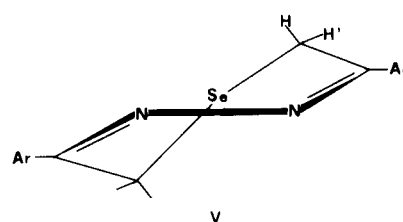
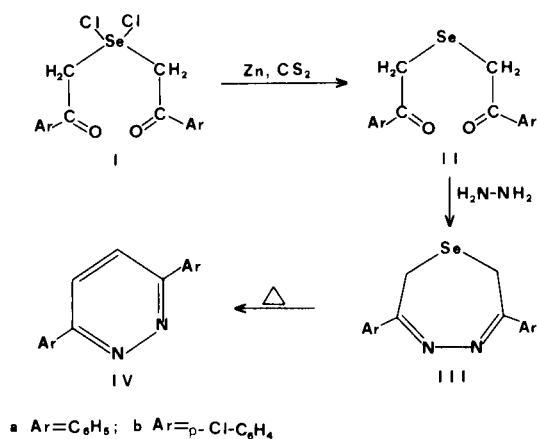
2,2''-Selenodiacetophenone (IIa) (1) and 2,2''-selenobis[4'-chloroacetophenone] (IIb) obtained by reduction of the corresponding bis(dichloroselenoacetophenone) (Ib) (2) with zinc in carbon disulfide (1), readily reacted at room temperature with equimolar amounts of hydrazine yielding a new heterocycle, 2,7-dihydro-1,4,5-selenadiazepine (III).

This new heterocycle failed to form bromo derivatives with bromide in ether or in acetic acid, acetyl derivatives, and generally did not demonstrate any peculiar reactivity. The infrared spectra of III showed no absorption in the  $3\ \mu$  region for neither the solid nor its solution in carbon tetrachloride, and nmr spectra showed no signal attributable to an NH proton which is consistent with the 2,7-dihydro structure of compounds III.

The spectrum of IIIa was measured in deuteriochloroform and showed a multiplet at  $\delta$  8.02-7.33 for aromatic protons and two doublets centered at  $\delta$  3.30 and 3.75 ( $J = 11.2$  Hz) for the H and H' methylenic protons. The nmr spectrum of IIIb showed two doublets centered at  $\delta$  7.83 and 7.43 ( $J = 8.5$  Hz) for the H and H' *para*-substituted benzene aromatic protons and an AB pattern with two doublets centered at  $\delta$  3.73 and 3.24 ( $J = 11.3$  Hz) for the H and H' protons in the ratio of 10:2:2. These data demonstrate that the H and H' protons are magnetically nonequivalent as might be expected from the puckered nature of this seven-membered ring. Molecular models indicate that this ring, like the comparable ring of 2,7-dihydro-1,4,5-thiadiazepine (3), possesses a skew-boat conformation (V).

Both the 2,7-dihydro-3,6-diphenyl-1,4,5-selenadiazepine (IIIa) and the 2,7-dihydro-3,6-di-*p*-chlorophenyl-1,4,5-selenadiazepine (IIIb) underwent facile ring contraction when heated in ethylene glycol to afford the corresponding pyridazines which were shown to be identical (mixture

m.p., ir) with 3,6-diphenyl and 3,6-di-*p*-chlorophenylpyridazine (IV) obtained by independent syntheses (4,5). Briefly, the chemical and physical properties of this new heterocycle seem to be similar to those of the comparable ring, 2,7-dihydro-1,4,5-thiadiazepine (3,6,7), which is confirmed by all our data.



## EXPERIMENTAL

All melting points (Kofler) are uncorrected. Ir: Perkin-Elmer Infracord 137 spectrophotometer; uv: *n*-hexane: Beckmann DB (with recorder) spectrophotometer; nmr: Jeol C-60H spectrometer (TMS as internal reference). Mass spectra were registered on a Hitachi Perkin-Elmer spectrometer.

2,2''-Selenobis(4'-chloroacetophenone) (IIb).

Zinc powder (10 g.) was added to a solution of dichlorobis(*p*-chlorophenacyl)selenium (10 g.) (Ib) (2) in carbon disulfide (800 ml.) and the mixture was heated under reflux for three days. After filtration and removal of the solvent under reduced

pressure, a pale yellow solid was obtained which was recrystallized from ethanol yielding 8.2 g., m.p. 108-110°.

*Anal.* Calcd. for  $C_{16}H_{12}Cl_2O_2Se$ : C, 49.74; H, 3.10. Found: C, 49.57; H, 3.01.

#### 3,6-Diphenyl-2,7-dihydro-1,4,5-selenadiazepine (IIIa).

Hydrazine hydrate (0.5 g.) (0.01 mole) was added to a solution of 2,2'-selenodiacetophenone (IIa) (3.17 g.) (0.01 mole) (1) in acetic acid (25 ml.) and the mixture was stirred overnight. The resulting precipitate (1.9 g.) was collected and recrystallized from ethanol, yellow scales, m.p. 194-195°; uv (*n*-hexane)  $m\mu$ ,  $\lambda$  max 322 (sh) and 274; nmr (deuteriochloroform)  $\delta$  8.02-7.33 (m, 10H, aromatic), 3.75 and 3.30 2x (d, 2H,  $CH_2$ ) ( $J \cong 11.2$  Hz). Mass spectrum 314 ( $M^+$ ), 231, 211, 182, 130, 116, 103, 91, 77 m/e.

*Anal.* Calcd. for  $C_{16}H_{14}N_2Se$ : C, 61.34; H, 4.45; N, 8.91. Found: C, 61.52; H, 4.48; N, 8.94.

#### 3,6-Diphenylpyridazine (IVa).

Refluxing 0.5 g. of IIIa in 15 ml. of ethylene glycol for three hours afforded in high yield a product, m.p. 222°, which was identical with an authentic sample of 3,6-diphenylpyridazine (4).

#### 3,6-Di-*p*-chlorophenyl-2,7-dihydro-1,4,5-selenadiazepine (IIIb).

Hydrazine hydrate (0.5 g.) (0.01 mole) was added to a solution of IIb (3.86 g.) (0.01 mole) in acetic acid (30 ml.) and the mixture was stirred overnight or heated for a few minutes to

yield a precipitate (3.2 g.) which was recrystallized from benzene-petroleum ether, m.p. 213-215°; uv (*n*-hexane)  $m\mu$ ,  $\lambda$  max 324 (sh) and 278; nmr (deuteriochloroform)  $\delta$  7.83 and 7.43 2x (d, 4H, aromatic) ( $J \cong 8.5$  Hz), 3.73 and 3.24 2x (d, 2H,  $CH_2$ ) ( $J \cong 11.3$  Hz). Mass spectrum 383 ( $M^+$ ), 300, 246, 217, 182, 151, 137, 101, 75 m/e.

*Anal.* Calcd. for  $C_{16}H_{12}Cl_2N_2Se$ : C, 50.26; H, 3.13; N, 7.31. Found: C, 50.25; H, 3.31; N, 7.29.

#### 3,6-Di-*p*-chlorophenylpyridazine (IVb).

Compound IIIb (0.5 g.) was heated under reflux for three hours with 15 ml. of ethylene glycol affording a product, m.p. 264°, which was identical with an authentic sample of 3,6-di-*p*-chlorophenylpyridazine (5). This pyridazine had been incorrectly reported as 2,5-di-*p*-chlorophenylpyridazine.

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