

*Perhydroanthracene*, *m.p.* 50°C. For this, the most recently isolated of the perhydroanthracenes, with the *trans-anti-trans* configuration, there is no possibility of an all chair conformation. The alternatives are between a model in which the centre ring is of the formal boat shape and one in which one has the staggered boat form.

On the basis of the observed mean C—C bond lengths and CCC bond angles two models were calculated and the corresponding theoretical radial distribution curves. It was quite evident that the formal boat structure failed to match up with the experimental r.d. curves, whereas the staggered boat conformation gave good correlation in all regions and represents the correct structure.

The results of the entire series of investigations are presented in Table 1, together with those for cyclohexane.<sup>12</sup> It is interesting to note that the C—C bond distances in the fused ring compounds are consistently longer than that found for cyclohexane.

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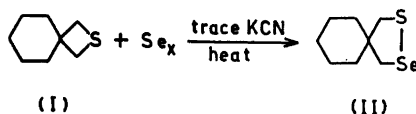
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## Formation of the 1-Thia-2-selenacyclopentane Ring System from the Thiacyclobutane Ring

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Hitherto only two substances have been prepared in which sulphur and selenium are neighbouring atoms in a small saturated ring system,<sup>1,2</sup> namely 1-thia-2-selenacyclopentane-4-carboxylic acid<sup>1</sup> and 4-(aminomethyl)-1-thia-2-selenacyclopentane.<sup>2</sup> For both the synthesis was rather laborious. A new substance (II) belonging to this class of compounds has now been synthesized in a simple but unusual way. On heating 2-thiaspiro-[3.5]-nonane\* (I) with elemental selenium to 180–190° for 16 h in diethylene glycol containing a trace of potassium cyanide, a selenium atom is incorporated in the thiacyclobutane ring and 2-thia-3-selenaspiro-[4.5]-decane (II) is formed in 75 % yield. The product is nicely crystalline and has the characteristic orange-red colour of the thiaselenacyclopentanes.



The absorption spectrum is given in Fig. 1 along with the spectra of the corresponding disulphide and diselenide. The close similarity between these spectra and those obtained for the carboxylic acids described earlier<sup>1</sup> constitutes a good proof for the structure given to our new compound.

Further, the NMR-spectrum at 60 Mc/s, of (II) shows three peaks with intensity ratio 1:1:5. The stronger peak, originating from the protons in the six-membered ring, appears at 1.28 ppm ( $\delta$ , relative

\* Nomenclature according to The Ring Index, 2nd Ed. Washington 1960.

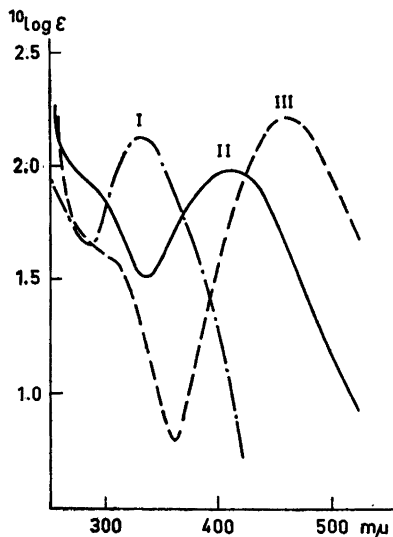


Fig 1. Ultraviolet spectra of 2,3-dithiaspiro-[4.5]-decane (I), 2-thia-3-selenaspiro-[4.5]-decane (II) and 2,3-diselenaspiro-[4.5]-decane (III) in cyclohexane solution.

tetramethylsilane) in about 30 % benzene solution. The signals from the protons in the five-membered ring are clearly separated, and occur at 2.65 and 2.81 ppm ( $\delta$ ). This splitting must be due to the difference in the chemical shifts of the protons in the groups  $-\text{CH}_2\text{-S-}$  and  $-\text{CH}_2\text{-Se-}$ , respectively, since the spectra of the corresponding disulphide and diselenide show only one peak each in the region in question. Further work is being carried out on the NMR-spectra of sulphur and selenium compounds.

The starting material (I) was first prepared by Backer and Tamsma<sup>3</sup> from 1,1-bisbromomethyl-cyclohexane and  $\text{Na}_2\text{S}$ . We found that (I) is more conveniently synthesized from cyclohexane-1,1-dimethylbenzenesulphonate.<sup>4</sup> By heating this sulphonate with aqueous  $\text{Na}_2\text{S}$  in diethylene glycol, the thiacyclobutane (I) was obtained in 56 % yield. Further studies of the reaction between selenium and thiacyclobutane derivatives are in progress. An analogous attempt to treat 2-selenaspiro-[3.5]-nonane with sulphur resulted only in polymer formation.

*Experimental.* 2-Thiaspiro-[3.5]-nonane (I). A solution of 21.2 g (0.05 mole) of cyclohexane-1,1-dimethylbenzenesulphonate in 200 ml diethylene glycol was heated to 100°. One third of a solution of 12 g (0.05 mole)  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  in 15 ml of water was added and heating was continued to 150°. A mixture of water, diethylene glycol and product began to distil off. The remaining  $\text{Na}_2\text{S}$  solution was added dropwise during 1 h and then 50 ml of water was added during the next 2 h. At the same time the distillate was being collected. The distillate was extracted four times with 50 ml of ligroin, the extracts washed twice with water, dried over  $\text{CaCl}_2$  and the solvent distilled off. The remaining light yellow oil was fractionated yielding 4 g. (0.028 mole) of 2-thiaspiro-[3.5]-nonane as a colorless liquid, b.p. 87–90°/13 mm Hg,  $n_D^{22} = 1.5170$ . Yield: 56 %. (Literature value: b.p. 96°/18 mm Hg).

2-Thia-3-selenaspiro-[4.5]-decane (II). To 4 g (0.028 mole) of 2-thiaspiro-[3.5]-nonane and 3 g (0.039 mole) of gray selenium powder in 250 ml of diethylene glycol was added a trace of KCN and the mixture was heated with stirring to 180–190° for 16 h. After cooling the mixture was extracted six times with 50 ml of ligroin, the combined extracts washed twice with water, dried over  $\text{CaCl}_2$  and the ligroin distilled off. The remaining red oil crystallized upon cooling. 4.6 g (0.021 mole) made a yield of 75 %. Fractionation yielded the analytically pure product b.p. 109–112°/0.1 mm Hg m.p. 29–30° in orange-red needle-shaped crystals. (Found: C 43.26; H 6.40; Se 36.00; Calc. for  $\text{C}_8\text{H}_{14}\text{SSe}$  (221.23): C 43.43; H 6.38; Se 35.69).

The selenium analysis were carried out according to Fredga.<sup>5</sup>

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