METHYL-SUBSTITUTED HETEROCYCLIC BASES CONTAINING CONDENSED SELENONAPHTHENE RINGS

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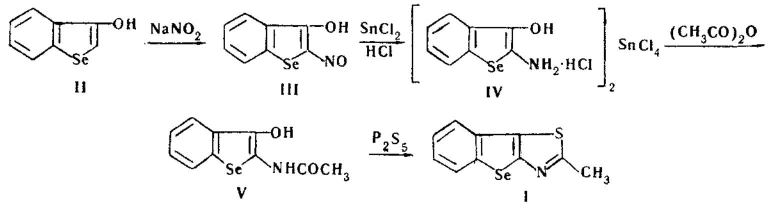
The synthesis of 2-methylselenonaphtheno[2,3-d]thiazole and 2-methylselenonaphtheno[2,3-d]-oxazole is described.

Methyl-substituted heterocyclic bases (containing a selenonaphthene ring) condensed with thiazole, oxazole, or pyridine rings are not described in the literature. At the same time, such bases may serve as the starting compounds for the synthesis of various classes of polymethine dyes.

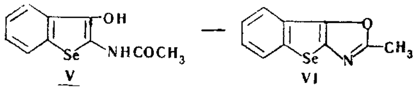
2-Methylselenonaphtheno[2,3-d]thiazole (I) was synthesized from 3-hydroxyselenonaphthene (II) [1-4] via the scheme



2-Nitroso-3-hydroxyselenonaphthene (III) was synthesized by nitrosation of 3-hydroxyselenonaphthene (II). The double tin salt of 2-amino-3-hydroxyselenonaphthene hydrochloride (IV), from which 2-acetamido-3-hydroxyselenonaphthene (V) was obtained by acetylation with acetic anhydride, was obtained by reduction of III with stannous chloride in concentrated hydrochloric acid.

Base I, which readily forms a picrate and quaternary salt, is obtained in 37% yield by heating V with phosphorus pentasulfide.

2-Methylselenonaphtheno[2,3-d]oxazole (VI) was obtained by heating V at 220-240°C.



EXPERIMENTAL

3-Hydroxyselenonaphthene (II). This was obtained by cyclization of o-carboxyphenylselenoglycolic acid [1-3] in acetic anhydride in the presence of anhydrous sodium acetate at 100-105° with subsequent hydrolysis of the 3-acetoxyselenonaphthene formed by heating with 10% sodium hydroxide. The yield of colorless needles (from ethanol) with mp 70-71° was 91% (mp 76-77.70° [2-4]).

2-Nitroso-3-hydroxyselenonaphthene (III). This was obtained in 93% yield by the reaction of sodium nitrite with II. The yellow needles (from benzene) had mp 154-155° (154-155° [5]).

Double Tin Salt of 2-Amino-3-hydroxyselenonaphthene Hydrochloride (IV). Pulverized III [22.6 g (0.1 mole)] was added with vigorous stirring to a solution of 135 g (0.7 mole) of stannous chloride in 180 ml of concentrated hydrochloric acid at 40-42° in the course of 1 h. At the end of the addition the mixture was

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stirred at 42-44° for 1 h and at 45-47° for 2 h. The precipitate that formed on cooling of the mixture was removed by filtration, washed with small amounts of ethanol and ether, and air-dried to give 30 g (80%) of light-yellow prisms (from anhydrous ethanol).

2-Acetamido-3-hydroxyselenonaphthene (V). A solution of 22 ml of acetic anhydride in 40 ml of ether was added to a suspension of 37.8 g (0.05 mole) of IV in 220 ml of water at 0-5° with vigorous stirring. A solution of 50 g of sodium hydroxide in 100 ml of water was then added in small portions to the mixture at 5-10°. At the end of the addition the mixture was stirred for 1 h at the same temperature and for another hour at room temperature. The ether was removed with an air stream, the mixture was filtered, and the filtrate was acidified, with cooling, with dilute (1:1) hydrochloric acid. The precipitate was removed by filtration, washed with water, and dried to give 17 g (67%) of rose prisms (from 50% ethanol in the presence of activated charcoal) with mp 167-168°. Found %: N 5.34, 5.38. $C_{10}H_9NO_2Se$. Calc. %: N 5.51.

2-Methylselenonaphtheno[2,3-d]thiazole (I). A thoroughly pulverized mixture of 15 g (0.06 mole) of V and 15 g (0.067 mole) of phosphorus pentasulfide was heated for 6-8 min at 130-140°. The dark-brown melt was treated with 120 ml of warm water, and the mixture was cooled, made alkaline with 25% sodium hydroxide, and steam-distilled. The base was extracted from the distillate with ether. After distillation of the solvent from the ether extracts (dried over calcined potassium carbonate), the residue was crystallized from petroleum ether to give 5.6 g (37%) of colorless plates with mp 73-74°. Found %: C 47.49, 47.54; N 5.52, 5.75; S 12.76, 12.83. $C_{10}H_7NSSe$. Calc. %: C 47.63; N 5.55; S 12.71. The picrate was obtained as light-yellow prisms (from anhydrous ethanol) with mp 146-147°. Found %: N 11.49, 11.56. $C_{16}H_{10}N_4O_7SSe$. Calc. %: N 11.65. The ethiodide was obtained as colorless plates (from anhydrous ethanol) with mp 201-202°. Found %: N 3.34, 3.49. $C_{12}H_{12}INSSe$. Calc. %: N 3.43.

2-Methylselenonaphtheno[2,3-d]oxazole (VI). Compound V [15 g (0.06 mole)] was gradually heated to 220-240° (a mixture of water and acetic acid distilled at this temperature), and the reaction mass was held at 230-240° for 15-20 min and vacuum-distilled. The fraction with bp 180-190 (5 mm) was collected to give 2.8 g (20%) of a light-yellow oil which began to crystallize on cooling. Crystallization from petroleum ether gave colorless plates with mp 53-54°. Found %: C 50.69, 50.79; N 5.74, 5.86. $C_{10}H_7NOSe$. Calc. %: C 50.87; N 5.93.

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