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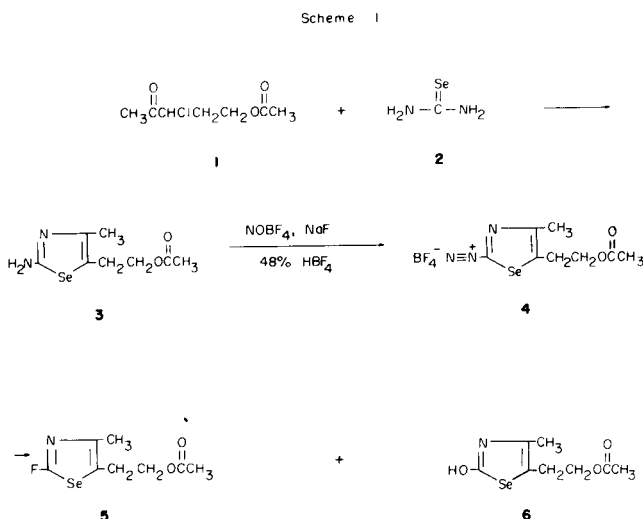
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Diazotization of 5-(acetoxyethyl)-2-amino-4-methylselenazole with nitrosoborofluoride in the presence of sodium fluoride in fluoboric acid solution furnishes 5-(acetoxyethyl)-2-fluoro-4-methylselenazole and the corresponding 2-hydroxy compound. Despite low yields, this was the first time that a Sandmeyer-Schiemann reaction has been carried out successfully with 2-aminoselenazoles.

J. Heterocyclic Chem., **19**, 1245 (1982).

In connection with another problem 5-acetoxyethyl-2-fluoro-4-methyl-selenazole was required as an intermediate (2). We proposed to use the method shown in Scheme I despite that fact that it had been reported (3,4) that Sandmeyer type reactions of 2-aminoselenazoles (5) failed completely, elemental selenium being obtained as the only isolatable product.



5-Acetoxy-3-chloro-2-pentanone (2) was condensed with selenourea (5) to give the 2-aminoselenazole, **3**, which was dissolved in a solution of sodium fluoride in 48% tetrafluoroboric acid and treated with nitrosium tetrafluoroborate. The presence of the diazonium species, **4**, was detected with the aid of β -naphthol (6). On work-up the reaction mixture afforded, in addition to some elemental Se, the 2-fluoroselenazole, **5**, (17%) and the hydroxy-selenazole, **6**, (26%). These new selenazoles, **5**, and **6** were probably formed by the reaction of the unstable diazonium salt, **4**, with F^- and water respectively. Although the yields were not satisfactory, to our knowledge this is the first time that a Sandmeyer-Schiemann type reaction has been carried out successfully with 2-aminoselenazoles.

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. ^1H nmr spectra were recorded on a Varian HA 100 spectrometer with TMS as the internal standard. Mass spectra were obtained using a Joel JMS-O1SC mass spectrometer at 70 eV.

5-(Acetoxyethyl)-2-amino-4-methylselenazole (3).

A solution of **1** (2) (7.86 g, 0.044 mole) in 40 ml of absolute ethyl alcohol was treated with selenourea, **2**, (0.6 g, 0.049 mole) and heated under reflux on a steam bath with stirring for 15 minutes. To the hot solution was added 20 ml of absolute alcohol and solid anhydrous sodium acetate to pH 7. The hot solution was filtered through Super-Cel and the filtrate was concentrated under reduced pressure to leave a semi-solid. This was treated with 20 ml of acetonitrile and refiltered. The filtrate was concentrated and the oily residue was chromatographed on a Waters Prep 500 using methylene chloride-ethyl acetate (1:4) as the solvent system. There was obtained 7.2 g (68%) of **3**. After crystallization from ether-ethyl acetate it melted at 115-116°; ^1H nmr (deuteriochloroform): δ 2.07 (s, CH_3 , 3H), 2.10 (s, CH_3 , 3H), 2.94 (t, CH_2 , 2H), 4.17 (t, CH_2 , 2H), 6.07 (broad, NH_2 , 2H); ms: 248, 246 (M^+).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2\text{Se}$: C, 38.88; H, 4.89; N, 11.33. Found: C, 39.08; H, 4.92; N, 11.25.

5-Acetoxyethyl-2-fluoro-4-methylselenazole (5) and 5-Acetoxyethyl-2-hydroxy-4-methylselenazole (6).

A solution of **3** (2.96 g, 0.012 mole) in 15 ml of 48% fluoroboric acid was cooled in an ice-methanol bath and treated with sodium fluoride (0.5 g, 0.012 mole) and nitrosyl tetrafluoroborate (1.44 g, 0.0124 mole). The solution was stirred for 45 minutes, before the reaction mixture was treated with 50 ml of chloroform. The aqueous layer was extracted with chloroform (3 \times 30 ml). The combined organic layers were washed with water (3 \times 25 ml). Red metallic selenium was present in the aqueous washings. The organic layer was dried over anhydrous magnesium sulfate and the filtered solution was purified by chromatography on a dry silica gel column (7), 22 \times 1½" using 20% ethyl acetate in dichloromethane as the eluant. The less polar fraction afforded the fluoroselenazole, **5**, 0.5 g (16%); ^1H nmr (deuteriochloroform): δ 2.08 (s, CH_3 , 3H); 2.12 (s, CH_3 , 3H); 3.06 (dt, CH_2 , 2H, $J_{\text{F-H}} = 3-4$ Hz); 4.14 (t, CH_2 , 2H); ms: 251, 249. (M^+). An analytical sample prepared by kugelrohr distillation, boiled at 50° (0.01 mm).

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{FNO}_2\text{Se}$: C, 38.42; H, 4.03; N, 5.60; F, 7.60. Found: C, 38.55; H, 4.12; N, 5.56; F, 7.51.

In another run the more polar fraction, **6**, 0.8 g (26%) was collected; ^1H nmr (deuteriochloroform): δ 2.04 (s, CH_3 , 3H); 2.08 (s, CH_3 , 3H); 2.86 (t, CH_2 , 2H); 4.18 (t, CH_2 , 2H); 9.9 (broad, OH, 1H); ms: 249, 247 (M^+). An analytical sample was prepared by crystallization from ether-hexane, mp 79-80°.

Anal. Calcd for $\text{C}_8\text{H}_{11}\text{NO}_3\text{Se}$: C, 38.73; H, 4.47; N, 5.65; Found: C, 38.79; H, 4.44; N, 5.71.

REFERENCES AND NOTES

(1) Address: Sterling-Winthrop Research Institute, Rensselaer, NY 12144. Taken from a thesis submitted by R. McGarry in partial fulfillment of the requirements of the M.S. degree.

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