[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TWO BIS-SELENIDES[1, 2]

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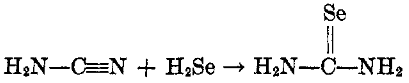
Complete details for the preparation of two new selenols by methods generally applicable to ordinary mercaptans are reported herewith. The Williamson synthesis was used to convert them to the corresponding *bis*-selenides. One method involved preparation of the selenol from sodium hydrogen selenide and an alkyl halide and the other is outlined in equations 1–5.

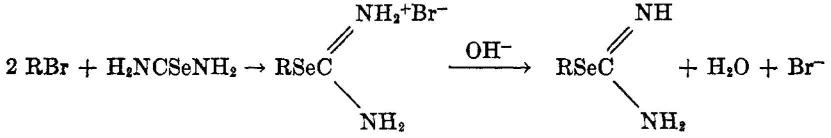
$$CaCN_2 + H_2O + H_2SO_4 \rightarrow CaSO_4 + H_2N{-}C{\equiv}N \tag{1}$$

(2)

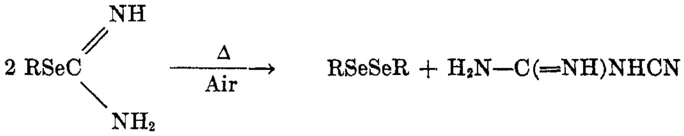


$$H_2N{-}C{\equiv}N + H_2Se \rightarrow H_2N{-}\overset{\overset{\displaystyle Se}{\|}}{C}{-}NH_2$$

(3)



(4)



$$RSeSeR \xrightarrow{LiAlH_4} 2\,RSeH \tag{5}$$

The selenols were converted to their sodium salts by reaction with sodium sand and then were coupled with the appropriate alkyl halide.

EXPERIMENTAL[3, 4]

Selenourea. This substance was prepared essentially according to Backer's (1) directions using hydrogen selenide generated from aluminum selenide.

2-Ethylhexylselenol. Powdered aluminum selenide from 60 g. of aluminum and 100 g. of selenium (2) was placed in a dry Erlenmeyer flask, and water was added dropwise, the generated hydrogen selenide being swept through a calcium chloride tube and a phosphorus pentoxide tube by a stream of nitrogen. The hydrogen selenide was absorbed in a solution of sodium ethoxide prepared from 20 g. (0.87 mole) of sodium and 200 ml. of *magnesium-dried* ethanol. To the resulting suspension of sodium hydrogen selenide was added 135 g. (0.70

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[2] Abstracted from a portion of WADC Technical Report 53-45, June, 1953. Released for publication by Mr. Harold Rosenberg, Senior Project Engineer, Polymer Section, Organic Materials Branch, Materials Laboratory, Directorate of Research.

[3] Melting points and boiling points are uncorrected.

[4] Microanalyses by Microtech Laboratories, Skokie, Illinois.

mole) of 2-ethylhexyl bromide, and the mixture was heated at 100° for 4 hr. Then it was filtered, and the alcohol was removed at the water pump. The residue was taken up in 500 ml. of ether and the ethereal solution was washed 4 times with water and was dried over magnesium sulfate. Evaporation afforded an oil which distilled at 68.5–70.0°/8.0 mm.; 87 g. (64.5%) 2-ethylhexylselenol, a colorless, dense oil with a nauseating odor. It was not analyzed, but was converted at once to the *bis*-selenide by coupling with hexamethylene dibromide.

A residue of about 25 g. remained in the still pot. Since this was considerably larger when ordinary absolute ethanol was employed, it was assumed to be the alkyl selenide, plus some alkyl diselenide formed by oxidation.

Cyclopentylmethylselenol. Method A. Substantially the same procedure as for the preceding 2-ethylhexylselenol was used with comparable results.

Method B. A slurry of 53 g. (0.43 mole) of selenourea in 40 ml. of water was added to 58 g. (0.36 mole) of cyclopentylmethyl bromide. The mixture was refluxed for 17 hr. and then was worked up in the same fashion as for regular mercaptans (3) to give 46 g. of a substance boiling at 133–135°/0.2 mm., the alkyl diselenide formed by oxidation. This material was added slowly to a solution of 3.4 g. (0.08 mole) of lithium aluminum hydride (4) in 350 ml. of anhydrous ether, and the mixture was refluxed for 40 min. The excess hydride was decomposed by cautious addition of water, and the precipitated salts were dissolved by addition of 5% hydrochloric acid. The solution next was steam-distilled, the aqueous layer then being extracted twice with benzene which then was added to the ether layer. After drying over magnesium sulfate and evaporation of the solvents there was obtained an oil which upon distillation afforded 34 g. (68%) of cyclopentylmethylselenol, b.p. 61–62°/13 mm. As with the 2-ethylhexyl compound, no analysis was attempted, conversion to the *bis*-selenide being carried out at once.

Coupling of the selenols with 1,6-dibromohexane. 2-Ethylhexylselenol. To 5.5 g. (0.24 mole) of sodium sand in 60 ml. of dry benzene was added 49.5 g. (0.256 mole) of the selenomercaptan in 40 ml. of dry benzene. After 1 hr. of stirring and refluxing the sodium had reacted completely, being replaced by a gelatinous precipitate. To the mixture then was added dropwise 29.3 g. (0.12 mole) of 1,6-dibromohexane in 30 ml. of dry benzene, and the mixture was refluxed for 7 hr., cooled and treated with 80 ml. of water. After separation the benzene layer was washed successively with water, 5% hydrochloric acid, 5% sodium bicarbonate, water, and then was dried over sodium sulfate. The light yellow oil which remained on removal of the benzene at the water pump distilled in two fractions: (a) 130–150°/0.2 mm. (9.5 g.), and (b) 189–194°/0.2 mm., 42.5 g. (76%). Redistillation of fraction (b) afforded a colorless oil, b.p. 183°/0.1 mm., n_{D}^{25} 1.5030: hexamethylene-*bis*(2-ethylhexyl selenide).

Anal. Calc'd for $C_{22}H_{46}Se_2$: C, 56.39; H, 9.90.
Found: C, 56.42; H, 10.00.

Cyclopentylmethylselenol. This substance (34 g., 0.21 mole) was similarly treated, using 4.4 g. (0.19 mole) of sodium and 23 g. (0.095 mole) of 1,6-dibromohexane in proportional volumes of dry benzene. There was obtained a yellow oil, b.p. 136–143°/0.2 mm., which was taken up in benzene and treated with 10% aqueous copper sulfate and then filtered from a large amount of flocculent precipitate. Subsequent distillation afforded 16.2 g. (42%) of a yellow oil, b.p. 175–180°/0.1 mm. The hexamethylene-*bis*(cyclopentylmethyl selenide) appeared to be quite unstable to heat.

Anal. Calc'd for $C_{18}H_{34}Se_2$: C, 52.94; H, 8.39.
Found: C, 52.20; H, 8.33.

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