

stored in a vacuum until used. To 185 g. of selenourea (m. p. 198, 22.57% N (calcd. 22.77)) 50 ml. of water was added, the air in the flask displaced with a stream of nitrogen and 103 g. of dimethyl sulfate added in a similar manner as used in the preparation of methyl isothiouraea sulfate.<sup>2,3</sup> After the initial reaction subsided the contents were heated with a low flame for twenty-five minutes. The contents of the flask set to a solid dark mass (color due to metallic selenium) before the heating was discontinued. After cooling, the solid mass was washed with 150 ml. of cold ethanol.

The compound was dissolved in about one liter of hot water (4-5 drops of 18 M sulfuric acid added) and the metallic selenium, which cleaved in the initial reaction, removed by filtering through a steam jacketed funnel.



Methyl isoselenourea sulfate ((H<sub>2</sub>NC=NH)<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>) crystallized on cooling. The first crop yielded 194 g. By reducing the volume to about 100 ml. at reduced pressure and addition of an equal volume of ethanol, an additional 42 g. was obtained. The yield was about 85%. The recrystallized compound melted at 205-207°.

*Anal.* Calcd. for C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>N<sub>4</sub>SSe<sub>2</sub>; N, 15.06; S, 8.61; Se, 42.43. Found: N, 15.12; S, 8.6; Se, 42.4.

When methyl isoselenourea sulfate was hydrolyzed with sodium hydroxide it did not give a good yield of methyl selenomercaptan, as expected from the behavior of the sulfur derivative.<sup>2,4</sup> The principal reaction product was a yellow oil which remained in the reaction mixture.

(2) Arndt, *Ber.*, **54**, 2236 (1921).

(3) Shildneck and Windus, "Organic Syntheses," **13**, 52 (1932).

(4) Windus and Shildneck, *ibid.*, **14**, 54 (1934).

SCHOOL OF CHEMISTRY  
N. D. AGR. COLLEGE  
FARGO, N. DAK.

RALPH E. DUNBAR

DEPARTMENT OF CHEMISTRY  
COLLEGE OF AGRICULTURE  
UNIVERSITY OF CALIFORNIA  
DAVIS, CALIFORNIA

E. P. PAINTER

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### Some New Selenium Ethers<sup>1</sup>

#### β-Hydroxyethyl Phenyl Selenide

After the air in a flask containing 350 ml. of absolute ethanol was displaced by nitrogen, 103 g. (1/2 mole) of phenyl selenomercaptan were added. An equivalent of sodium was then added in small pieces until dissolved. The flask was immersed in ice water and 84 g. of ethylene bromohydrin were added over a period of about five minutes. The reaction was quite vigorous. After cooling to room temperature a few drops of 12 M hydrochloric acid were added and a current of air was drawn through the solution to oxidize any unreacted phenylselenomercaptan

to the diselenide. The salt was filtered, washed with dry ether and the solution distilled *in vacuo*. The product collected at 152-156° at 18 mm. was redistilled. The fraction distilling at 152-153° at 16 mm. was 116 g., 87% of theoretical.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>OSe: Se, 39.26. Found: Se, 38.6.

When brominated in carbon tetrachloride an orange compound melting at 113° was obtained. The compound was unstable and therefore was not successfully recrystallized.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>OBr<sub>2</sub>Se: Se, 21.88; Br, 44.28. Found: Se, 22.9; Br, 43.8.

#### β-Hydroxyethyl Benzyl Selenide

This compound was prepared from sodium benzyl selenide<sup>2</sup> and ethylene bromohydrin by the same procedure as for β-hydroxyethyl phenyl selenide except the volume of alcohol per mole of sodium benzyl selenide was twice that used for the phenyl derivative. The compound distilled at 130-132° at 2 mm. The yield was about 70%.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>OSe: Se, 36.70. Found: Se, 36.5.

The compound gave an unstable bromine addition product.

#### β-(Phenylseleno)-diethylacetyl

To 25 ml. of absolute ethanol, 15.7 g. (0.1 mole) of freshly distilled phenylselenomercaptan were added. The flask was cooled and after 2.3 g. of sodium (added in small pieces) were dissolved, 16 g. of β-chloro diethylacetal were added dropwise. The reaction mixture was warmed and refluxed gently for one hour. The flask was cooled and the contents were poured into 300 ml. of water. The water was made alkaline with sodium hydroxide. The lower layer, the acetal, was taken up in ether and the water was extracted with ether. The combined ether solutions were dried over anhydrous sodium sulfate and distilled at reduced pressure. β-Phenylselenodiethylacetal, b. p. 153-155° at 17 mm., straw yellow color, was obtained in 60% yield. When redistilled nearly all the product was collected at 153-153.5° at 17 mm.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>Se: Se, 28.90. Found: Se, 28.7.

The acetal gave an unstable bromine addition compound of orange yellow crystals. After hydrolyzing the acetal with N sulfuric acid, the aldehyde was treated with ammonia and hydrogen cyanide and the amino nitrile hydrolyzed with hydrochloric acid. The amino acid, β-(phenylseleno)-alanine,<sup>2</sup> was isolated in a yield of about 10% based on the acetal.

ABBOTT LABORATORIES  
NORTH CHICAGO, ILLINOIS  
DEPARTMENT OF CHEMISTRY  
COLLEGE OF AGRICULTURE  
UNIVERSITY OF CALIFORNIA  
DAVIS, CALIFORNIA

FLOYD C. MCINTIRE

E. P. PAINTER

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(2) Painter, *THIS JOURNAL*, **69**, 229 (1947).