

difference in color is undoubtedly due to a difference in the state of division of the two samples.

*Analyses.* Calc. for  $C_{29}H_{26}O_2N_4S$ : N, 11.33. Found: 11.61, 11.42.

### Summary

1. The compounds formed by the reaction of alcoholic ammonia on chloro-aceto-ethylanilide and chloro-aceto-phenylanilide have been identified and certain of their derivatives prepared.

2. Attempts to convert amino-aceto-phenylanilide into the corresponding isothiocyanate were unsuccessful.

3. The anomalous behavior of amino-aceto-phenylanilide dithiocarbamate toward mercury and silver salts has been noted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,  
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## RESEARCHES ON SELENIUM ORGANIC COMPOUNDS III. THE PREPARATION OF A SELENIUM DERIVATIVE OF CINCHOPHEN TYPE

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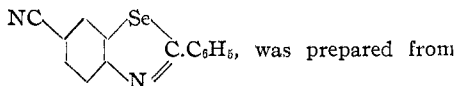
### Introductory

Bogert and Abrahamson<sup>1</sup> have described the synthesis of 2-phenyl-benzothiazole-6-carboxylic acid from 2-phenyl-6-aminobenzothiazole, and have pointed out its structural relationship to Cinchophen (Atophan) and the possibility of its possessing useful physiological properties.

Pending the carrying out of pharmacological tests on the sulfur compound, it seemed to us worth while to prepare the analogous selenium compound, so that the properties of the two might be compared, and this brief contribution records that synthesis. As was the case with the sulfur compound, so here too it was found impossible to obtain either the nitrile or the free acid in crystalline form, and final purification was accomplished through the methyl ester.

### Experimental Part

2-Phenyl-6-cyano-benzoselenazole,



the corresponding 6-amino derivative<sup>2</sup> by the Sandmeyer reaction. From 10 g. of the amine, 12 g. of crude nitrile was obtained in the form of a brownish powder, which decomposed at 145–150° with previous sintering, and which defied all attempts to crystallize it. By repeated solution in alcohol and re-precipitation with water, it was

<sup>1</sup> Bogert and Abrahamson, *THIS JOURNAL*, **44**, 826 (1922).

<sup>2</sup> Bogert and Chen, *ibid.*, **44**, 2355 (1922).

changed into a pale yellowish, coarse powder, which was soluble in hot ethyl or *n*-butyl alcohol, acetone, carbon tetrachloride or benzene.

**2-Phenyl-benzoselenazole-6-carboxylic Acid.**—The crude nitrile (12 g.) was boiled for 22 hours under a reflux condenser with a mixture of 50 cc. of concd. sulfuric acid and 25 cc. of water. The solution was then cooled, diluted with 100 cc. of water, the precipitate collected, washed with water, suspended in warm *N* potassium hydroxide solution and again filtered. The clear filtrate was acidified with hydrochloric acid, which precipitated the selenazole acid. This precipitate was removed, washed and dried; yield, 4.9 g., or 36%. It appeared then as a pale brownish-yellow powder, which we were unable to crystallize and which was further purified, therefore, by repeated solution in alkali and re-precipitation by acid. The final product decomposed at 170–180°, and was very slightly soluble in water, although dissolving more freely in hot alcohol, ethyl acetate, acetone or benzene.

**Methyl Ester.**—From the acid, absolute methyl alcohol and dry hydrogen chloride, this ester was easily prepared. The crude product was treated with sodium carbonate solution, then with decolorizing carbon (Norite), and was crystallized repeatedly from alcohol. As thus purified, it formed glistening, pale yellowish flakes; m. p., 164.5–165.5° (corr.); yield, 10%. The poor yield was due to losses incident to purification for analysis.

*Analysis.* Calc. for  $C_{16}H_{11}O_2NSe$ : C, 56.93; H, 3.48. Found: C, 56.54; H, 3.57.

The ester dissolved more or less readily in ethyl or *n*-butyl alcohol, acetone, benzene or glacial acetic acid.

It was prepared also from the crude nitrile by digesting the latter with a mixture of equal weights of methyl alcohol and concd. sulfuric acid, but the result was less satisfactory and the product consisted of a mixture of the ester and free acid.

**Potassium Salt.**—One g. of the pure methyl ester was dissolved in 20 cc. of alcohol and 3 cc. of a 20% solution of potassium hydroxide in alcohol was added. The potassium salt separated immediately as a fine, granular precipitate of faint pinkish shade. It was washed with alcohol and dried; yield, 50%.

*Analysis.* Calc. for  $C_{16}H_9O_2NSeK$ : C, 49.38; H, 2.37. Found: C, 49.14; H, 2.60.

It was quite readily soluble in alcohol, and dissolved in water to the extent of 1%. An aqueous solution gave precipitates with the following ions:  $NH_4^+$ ,  $Mg^{++}$ ,  $Ca^{++}$ ,  $Ba^{++}$ ,  $Al^{+++}$ ,  $Fe^{+++}$ ,  $Ni^{++}$ ,  $Cu^{++}$  and  $Pb^{++}$ .

### Summary

1. A selenium derivative of Cinchophen type, 2-phenyl-benzoselenazole-6-carboxylic acid, structurally akin to the 2-phenylbenzothiazole-6-carboxylic acid of Bogert and Abrahamson,<sup>1</sup> has been prepared from 2-phenyl-6-amino-benzoselenazole, together with its methyl ester.

2. The solubility of the potassium salt in water is approximately 1%, and this salt dissolves freely in alcohol. Its physiological properties have not been determined as yet.

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