2. The pharmacological examination of the latter substance indicates that the -onium element is significant in determining the stimulating, nicotine effect.

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[Contribution from the Chemical Laboratory of Johns Hopkins University]

SOME DERIVATIVES OF ETHYL SELENOMERCAPTAN

By Edwin H. Shaw, Jr.,[1] and E. Emmet Reid

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Introduction

The original object in taking up the study of ethyl selenomercaptan was to obtain selenium compounds similar to sulfonal.[2] This object was not attained because the mercaptole skeleton $R_2>C<(SeC_2H_5)_2$ is broken up by oxidation. Owing to the fact that very little study has been made of derivatives of ethyl selenomercaptan, it was considered advisable to broaden the scope of the investigation, and study several reactions of ethyl selenomercaptan.

Historical

Ethyl selenomercaptan was first prepared by Siemens[3] in 1847, who proved his product to be a mercaptan by allowing it to react with mercuric oxide to form the mercury-ethyl selenomercaptide, $(C_2H_5Se)_2Hg$. Tschugaeff[4] has also studied the reactions of aliphatic selenomercaptans, preparing mercaptides and mixed aliphatic seleno-ethers. He also observed the fact that aliphatic selenomercaptans can be readily oxidized by atmospheric oxygen to the corresponding diselenides. No further work has been reported on the reactions of aliphatic selenomercaptans.

Outline of the Present Investigation

I. The preparation of ethyl selenomercaptan.

$$C_2H_5NaSO_4 + NaSeH \longrightarrow C_2H_5SeH + Na_2SO_4$$

II. The condensation of ethyl selenomercaptan with ketones.

$$R_2>CO + 2HSeC_2H_5 \longrightarrow R_2>C<(SeC_2H_5)_2 + H_2O$$

III. The oxidation of the mercaptoles.

$$R_2>C<(SeC_2H_5)_2 + HNO_3 \longrightarrow 2C_2H_5SeO_2H.HNO_3$$

IV. The reaction of sodium ethyl selenomercaptide with β,β'-dichloroethyl sulfide, sulfoxide and sulfone.

$$S(CH_2CH_2Cl)_2 + 2NaSeC_2H_5 \longrightarrow S(CH_2CH_2SeC_2H_5)_2 + 2NaCl$$
$$OS(CH_2CH_2Cl)_2 + 2NaSeC_2H_5 \longrightarrow OS(CH_2CH_2SeC_2H_5)_2 + 2NaCl$$
$$O_2S(CH_2CH_2Cl)_2 + 2NaSeC_2H_5 \longrightarrow O_2S(CH_2CH_2SeC_2H_5)_2 + 2NaCl$$

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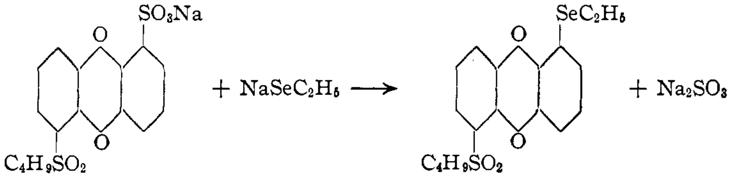
[1] From the Doctor's Dissertation of Edwin H. Shaw, Jr., 1925.

[2] Baumann, *Ber.*, **19**, 2808 (1886).

[3] Siemens, *Ann.*, **61**, 360 (1847).

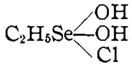
[4] Tschugaeff, *Ber.*, **42**, 49 (1909).

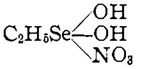
V. The reaction of sodium ethyl selenomercaptide with anthraquinone sodium sulfonates.

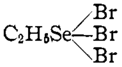


Results

Ethyl selenomercaptan has been found to resemble its sulfur analog in its condensation with ketones to form selenomercaptoles, $R_2>C<(Se_2H_5)_2$. Derivatives of acetone, methylethyl ketone and diethyl ketone have been obtained. Oxidation of any one of these yields the nitric acid compound of ethyl seleninic acid, $C_2H_5SeO_2H{\cdot}HNO_3$, quantitatively. It has been found better, however, to make this compound by oxidation of ethyl selenomercaptan. This is readily transformed into the hydrochloride, $C_2H_5SeO_2H{\cdot}HCl$, previously studied by Rathke.[5] Hydrobromic acid does not give the analogous hydrobromide, but ethylselenium tribromide, $C_2H_5SeBr_3$, instead. This is a new type of compound without analogy among sulfur derivatives. As the normal valence of selenium is four, these compounds probably have the structures


$C_2H_5Se\begin{cases}OH\\OH\\Cl\end{cases}$


$C_2H_5Se\begin{cases}OH\\OH\\NO_3\end{cases}$


$C_2H_5Se\begin{cases}Br\\Br\\Br\end{cases}$

With β,β'-dichloro-ethyl sulfide and the corresponding sulfone, reaction takes place readily, but with the sulfoxide much more slowly. In all three cases the compounds obtained, $(C_2H_5SeCH_2CH_2)S$, $(C_2H_5SeCH_2CH_2)_2SO$ and $(C_2H_5SeCH_2CH_2)_2SO_2$, are strictly analogous to those obtained by Helfrich and Reid[6] from ethyl mercaptan.

As Reid, Mackall and Miller[7] and Hoffman and Reid[8] found that mercaptans react readily with sodium α-anthraquinone sulfonate and the 1,5- and 1,8-disulfonates to give anthraquinone thio and di-thio ethers, the selenomercaptan was heated with the same salts under similar conditions. There were indications of a similar reaction, but selenomercaptan is such a powerful reducing agent that it reduces the anthraquinone sulfonates to the unreactive hydrol form before the desired reaction takes place to any considerable extent. In the case of sodium anthraquinone-1-butylsulfone-5-sulfonate the substitution is so rapid that anthraquinone-1-butylsulfone-5-ethyl-seleno-ether, $1{,}5\text{-}C_4H_9SO_2.C_{14}O_2H_6.SeC_2H_5$, is obtained.

[5] Rathke, *Ann.*, **152**, 217 (1869).

[6] Helfrich and Reid, THIS JOURNAL, **42**, 1218 (1920).

[7] Reid, Mackall and Miller, *ibid.*, **43**, 2104 (1921).

[8] Hoffman and Reid, *ibid.*, **45**, 1831 (1923).

Selenium was determined in these compounds by fusion with sodium peroxide in the Parr bomb followed by precipitation of the selenium as the element, as will be described in a separate paper.

Experimental Part

I. The Preparation of Ethyl Selenomercaptan

Aluminum selenide was prepared by the method of Moser and Doctor.[9] After several preparations, it was found that the following proportions gave the best results.

An intimate mixture of 200 g. of aluminum powder and 900 g. of powdered selenium was placed in a clay crucible just large enough to hold all the material. The mixture was ignited by means of magnesium ribbon and the crucible immediately covered. The preparation yielded 740 g. of aluminum selenide, which is 69% on the basis of the aluminum, and 67% on the basis of the selenium used.

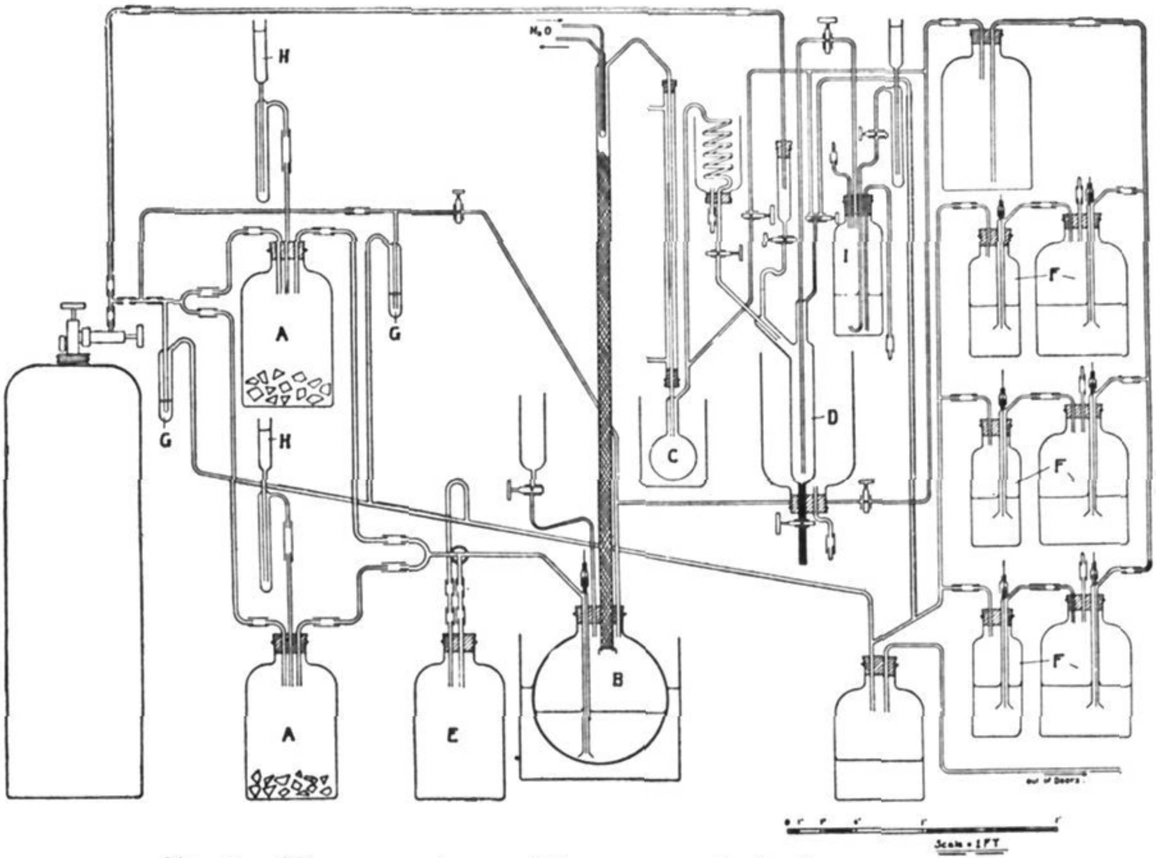


Fig. 1.—The apparatus used to prepare ethyl selenomercaptan.

In a preliminary experiment ethyl selenomercaptan was prepared by the method of Tschugaeff.[4] This method gave a 28% yield of the mercaptan but it involved much handling of the disagreeable product and was therefore discarded.

The method finally used was an adaptation of that described by Siemens.[3] A gas-tight apparatus was designed to avoid handling the selenomercaptan. Fig. 1 is a diagrammatic illustration of this apparatus.

[9] Moser and Doctor, *Z. anorg. allgem. Chem.*, **118,** 284 (1921).

A current of hydrogen from the tank is kept flowing through the apparatus continuously. Hydrogen selenide is generated in A by dropping water on aluminum selenide. About 350 g. of aluminum selenide was required for each run, 1000 cc. of 10% sodium hydroxide solution in B (which is a 5-liter flask) being completely saturated with hydrogen selenide. It is necessary to warm the water-bath towards the end of the process to facilitate dissolving the sodium selenide which is first precipitated. The solution is allowed to cool with a slow current of hydrogen selenide flowing through it. A solution of 400 g. of potassiumethyl sulfate in the minimum amount of water is now added, and the mixture in B distilled on the water-bath. The column, which is of the Hempel type, affords practically complete separation of the ethyl selenomercaptan from the water, diethyl selenide and diethyl diselenide also present. The distillate collects in C, whence it is redistilled on the water-bath to D, which is calibrated. The waste reactants in B are forced over into E by reversing the hydrogen current. The traps F contain 10% sodium hydroxide solution, and are arranged in triplicate to facilitate replacements, so that there will always be fresh traps ready when one is clogged by accumulation of sodium selenide. The traps G contain mercury whose depth is adjusted so that they will release any pressure developed by some of the tubes clogging before hydrogen selenide blows back through the trap funnels H. Both hydrogen selenide and ethyl selenomercaptan produce intense irritation of the passages of the nose and throat. They are also very poisonous. The operator should at all times avoid exposure to these compounds, and should make it a rule to use a gas mask arranged for breathing through 10% sodium hydroxide solution whenever such exposure is probable.

A series of ten runs gave an average yield of 40% of ethyl selenomercaptan based on the potassiumethyl sulfate. The best yield was 55% and the worst was 30%. The total amount of mercaptan prepared in ten runs was 1048 g.

II. The Condensation of Ethyl Selenomercaptan with Ketones

This reaction is similar to the reaction of sulfur mercaptans with ketones described by Baumann.[10] The reaction is carried out in the calibrated chamber D. A 10% excess of the ketone is taken and hydrochloric acid gas generated in I is used as the condensing agent. The chamber D is surrounded by ice water during the reaction, and a current of hydrogen chloride about one bubble per second is used. This slow rate avoids warming of the reactants, and consequent loss of product. The reaction is complete in about one hour. The mercaptole $R_2>C<(SeC_2H_5)_2$ is washed thrice with 10% sodium hydroxide solution, and twice with water. The yield of crude material in six runs averaged 97%. Condensations

TABLE I

ANALYSES AND PROPERTIES OF THE MERCAPTOLES

Compound	Percentage of selenium Calcd.	Found		Boiling point °C.	Mm.	d_0^0	d_{25}^{25}
$(CH_3)_2>C<(SeC_2H_5)_2$	61.26	60.85	60.87	81	4	1.4577	1.4329
$CH_3(C_2H_5)C<(SeC_2H_5)_2$	58.11	57.96	58.16	91.5	3.5	1.4294	1.4064
$(C_2H_5)_2>C<(SeC_2H_5)_2$	55.27	54.83	55.13	104.5	3.5	1.3825	1.3608

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[10] Baumann, *Ber.*, **18**, 887 (1885).

were carried out with acetone, methylethyl ketone and diethyl ketone. The properties of the condensation products are given in Table I. It may be noted that the boiling points increase regularly with the molecular weight and that the densities decrease with decreasing proportion of selenium in the compound.

III. Oxidation of the Mercaptoles

The mercaptoles were subjected to oxidation in an attempt to prepare the selenium analogs of sulfonal, trional and tetronal, but it was not possible to prepare any compounds of this type. Oxidation of either of the mercaptoles with nitric acid diluted with four volumes of water in the cold results in the rupture of the bond between the selenium atom and the carbon atom of the ketone and the formation of the nitric acid compound of ethylseleninic acid in quantitative yield. An aqueous solution of this compound was prepared by Rathke[5] as an intermediate stage in the preparation of $C_2H_5SeO_2H \cdot HCl$, but he did not isolate the compound, or assign to it any formula.

The Nitric Acid Compound of Ethylseleninic Acid, $C_2H_5SeO_2H \cdot HNO_3$.—This compound can be most readily prepared by the oxidation of ethyl selenomercaptan with nitric acid.

Cold, dil. nitric acid attacks the free selenomercaptan much less readily than the mercaptole, so it was necessary to use stronger nitric acid (1 volume of nitric acid diluted with 1 volume of water), which reacts vigorously with ethyl selenomercaptan to form $C_2H_5SeO_2H \cdot HNO_3$. The compound is obtained in crude form by evaporating the solution to a sirupy consistency on the water-bath, and stirring the molten mass while it cools to separate the excess of nitric acid and water. The compound is very soluble in water, being easily soluble in the cold in its own weight of water. It can be recrystallized from one-third its weight of water as thin, white plates; m. p., 80° (corr.). The compound is stable at ordinary temperatures, but when heated to 100° it gradually decomposes with the formation of a volatile oil with an extremely nauseating odor, causing dizziness and headache. The pure $C_2H_5SeO_2H \cdot HNO_3$ gave the following analyses.

Anal. Calcd.: Se, 38.77. Found: 38.56, 38.80.

The Hydrochloric Acid Compound of Ethylseleninic Acid, $C_2H_5SeO_2H \cdot HCl$.—This compound has been described by Rathke,[5] but no melting point was given. In this work the compound has again been prepared in order to compare it with the nitric acid compound.

When a concentrated aqueous solution of the nitric acid compound is treated with hydrochloric acid, a white crystalline precipitate of $C_2H_5SeO_2H \cdot HCl$ is formed in quantitative yield. The compound is immediately filtered off by suction, washed with ether and dried by drawing air through the material while it is still on the funnel. The compound prepared in this manner is quite pure; solution in water and reprecipitation with hydrochloric acid did not improve the product. The dry compound slowly decomposes at room temperature, becoming slightly brown or pink after eight or ten days. An aqueous solution of the compound decomposes rapidly with the formation of a volatile oil with an extremely nauseating odor, similar to that of the decomposition product of the nitric acid compound. This oil further decomposes with the deposition of free selenium. The pure substance $C_2H_5SeO_2H{\cdot}HCl$ has no definite melting point; it melts and decomposes at 100° to 107° depending on the rate of heating. When the heating is rapid (14° per minute), the compound melts at 107°, decomposing with gas evolution to yield a brown liquid. The pure compound gave the following analyses.

Anal. Calcd.: Se, 44.56; Cl, 19.95. Found: Se, 44.42, 44.44; Cl, 20.07, 20.21.

Ethylselenium Tribromide, $C_2H_5SeBr_3$.—On treatment with hydrobromic acid, the nitric acid compound of ethylseleninic acid yields a different sort of product. Instead of the $C_2H_5SeO_2H{\cdot}HBr$ that was expected, the product was ethylselenium tribromide. This is a new type of compound. There is no analogous sulfur compound.

Five g. of $C_2H_5SeO_2H{\cdot}HNO_3$ was dissolved in 5 cc. of water, and 20 cc. of carbon tetrachloride was added. On addition of 20 cc. of constant-boiling hydrobromic acid, a yellow crystalline precipitate was formed. This was filtered off by suction, washed once with carbon tetrachloride, and dried by drawing air through it on the funnel for 30 minutes. The yield of ethylselenium tribromide was 7.58 g., or 89%. The compound decomposes in the course of 10 or 12 hours to a dark oil which further decomposes to form free selenium. The pure substance has no definite melting point. It darkens around 50° and decomposes at about 73° when the rate of heating is 14° per minute. A Parr bomb fusion on the compound was exceedingly difficult because the compound ignites when mixed with sodium peroxide, but by careful addition of the material in small portions it was possible to fill the bomb without igniting the material. The pure compound gave the following analyses.

Anal. Calcd.: Se, 22.76; Cl, 68.89. Found: Se, 22.79, 22.72; Cl, 68.78, 69.04.

The Interaction of Hydriodic Acid and the Nitric Acid Compound of Ethylseleninic Acid.—Attempts to prepare an iodine compound analogous to the chlorine and bromine compounds described above were unsuccessful. The nitric acid compound of ethylseleninic acid and hydriodic acid yielded a very dark viscous oil that was not investigated.

The Methylseleninic Acid Compounds.—Wöhler and Dean[11] prepared a similar series of compounds related to methylseleninic acid, but they did not characterize them completely. On oxidation of $CH_3Se{\cdot}SeCH_3$ with nitric acid they obtained a compound melting at 122° which they described as CH_3SeO_3H but gave no analysis. This compound is probably $CH_3SeO_2H{\cdot}HNO_3$. In the case of the hydrochloric acid compound they give a formula which cannot readily be transformed to present nomenclature, $CH_3SeO_{2^1/_2}H{\cdot}Cl$. Their analysis fits the formula $CH_3SeO_2H{\cdot}HCl$ as closely as it fits the formula they assign. With hydrobromic acid they obtained a yellow crystalline compound to which they assigned no formula and with hydriodic acid they obtained a dark oil.

Oxidation of the Mercaptoles with Hydrogen Peroxide.—Oxidation of the mercaptoles with 3% hydrogen peroxide yields a solution of ethyl seleninic acid which can be concentrated to a thick sirup without crystalliz-

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[11] Wöhler and Dean, *Ann.*, **97**, 5 (1856).

ing. Addition of hydrochloric acid to this sirup causes the precipitation of the hydrochloric acid compound of ethyl seleninic acid, and addition of hydrobromic acid results in the precipitation of ethyl selenium tribromide. Concentration of the solution from the hydrogen peroxide oxidation in a vacuum desiccator at ordinary temperatures yields a very hygroscopic solid which is probably the free seleninic acid.

The Action of Free Halogens on the Mercaptoles.—By the action of free halogens on the mercaptoles, the bond between the selenium and the carbon is ruptured.

On passing chlorine into a carbon tetrachloride solution of the mercaptole, a crystalline precipitate of selenium tetrachloride is formed, identified by the fact that it fumes in moist air giving off hydrochloric acid to form the water-soluble selenious acid. Addition of excess bromine to a carbon tetrachloride solution of the mercaptole results in the precipitation of orange crystals of selenium tetrabromide, identified by comparison with selenium tetrabromide. Both compounds darken at about 90° and melt at 118°.

Anal. Calcd. for $SeBr_4$: Se, 19.86; Br, 80.14. Found: Se, 19.61, 19.52; Br, 83.58, 81.49.

Treatment of the mercaptoles in carbon tetrachloride solution, in ether solution, and in alcohol solution with the calculated amount of bromine in similar solution yielded on concentration of the solution at room temperature only viscous evil-smelling oils that were not investigated. Treatment of the mercaptole dissolved in carbon tetrachloride, in ether and in alcohol with the calculated amount of iodine in similar solution yielded on concentration at room temperature only viscous, evil-smelling oils that were not investigated. It was not possible to prepare any compounds of the type $RR'C(SeX_2C_2H_5)_2$.

The Action of Alkyl Halides on the Mercaptoles.—When the mercaptole is treated with the alkyl iodide in the proportion of two molecules of the alkyl iodide to one molecule of the mercaptole and in the presence or absence of piperidene as a catalyst, a very slow reaction takes place. Overnight a few crystals form, probably the selenonium compound. These are unstable and change to a viscous oil that was not investigated.

IV. The Reaction of Sodium Ethylselenomercaptide with β,β'-Dichloro-ethyl Sulfide, Sulfoxide and Sulfone

The reaction of sodium sulfur mercaptides with β,β'-dichloro-ethyl sulfide, sulfoxide and sulfone was reported by Helfrich and Reid.[12] Similar reactions have been carried out in the case of sodium ethyl selenomercaptide. When one equivalent of mustard gas is mixed with two equivalents of ethyl selenomercaptan and two equivalents of *N* alcoholic sodium hydroxide solution and the mixture is refluxed for 15 minutes, an abundant precipitate of sodium chloride is formed, interaction taking place in accordance with the following reaction: $S(CH_2CH_2Cl)_2 + 2NaSeC_2H_5 \longrightarrow S(CH_2CH_2SeC_2H_5)_2 + 2NaCl$. As a by-product in this reaction a solid amorphous substance was obtained in a yield of 5%. This substance

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[12] Ref. 6, p. 1221.

melts at 91.5° (corr.) and analysis shows that it contains two atoms of sulfur to three of selenium, giving the following values: sulfur: 13.96%, 13.58%; selenium: 50.24%, 50.11%. The molecular weight was determined by the rise in boiling point of an alcoholic solution and was found to be 506 ± 25. The following suggestion is made for a formula of this compound, no claim being made for correctness. Sulfur: 13.59%, selenium: 50.34%; molecular weight: 472: $Se(C_2H_4SC_2H_4SeC_2H_5)_2$.

In the case of mustard gas sulfone the reaction takes place just as readily. On the addition of water the sodium chloride dissolves and the reaction product precipitates.

The reaction is much slower in the case of mustard gas sulfoxide. The sodium chloride precipitates only on continued refluxing. The material was refluxed for two hours, when an abundant precipitate of salt formed. On addition of water, no product separated, because the sulfoxide compound is soluble in water. On concentration of the water solution an oil separated which could not be distilled at 4 mm. and which did not solidify in freezing mixture. Since the compound could not be purified, analysis was run on the crude material. The analysis was close enough to justify the formula. The sulfoxide compound is miscible in all proportions with alcohol. The sulfide and sulfone compounds can be recrystallized from alcohol. The properties of the three products are given in condensed form in Table II.

TABLE II

ANALYSES AND PROPERTIES OF DERIVATIVES OF DICHLORO-ETHYL SULFIDE, SULFOXIDE AND SULFONE

Compound	Percentage selenium Calcd.	Found		M. p., °C. (corr.)	B. p., °C.	d_{25}^{25}	Yield, %
$(C_2H_5SeC_2H_4)_2S$	51.99	51.79	51.90	15	171°/4 mm.	1.4724	63
$(C_2H_5SeC_2H_4)_2SO$	49.40	45.25	...	..	decomposes	....	..
$(C_2H_5SeC_2H_4)_2SO_2$	47.05	47.14	47.10	72.5	....	....	84

V. The Reaction of Sodium Ethylselenomercaptide with Anthraquinone Sodium Sulfonates

The reactions of anthraquinone sodium sulfonates with mercaptans described by Reid, Mackall and Miller[7] and by Hoffman and Reid[8] were tried with ethyl selenomercaptan. Owing to the fact that ethyl selenomercaptan is a good reducing agent, in most cases the anthraquinone compound was reduced to the non-reactive hydrol and no seleno-ether was obtained. The following sodium salts yielded no seleno-ethers: anthraquinone 1-sulfonate, 1,5- and 1,8-disulfonates, 1-butylsulfide and 1-butylsulfone-8-sulfonate, and 1-butylsulfide-5-sulfonate. With anthraquinone 1-butylsulfone-5-sodium sulfonate, noted for its reactivity, anthraquinone 1-butylsulfone-5-ethyl selenide was obtained as shining bronze-like scales in yield of 30%. On recrystallization from water, the compound was obtained as deep red needles. The corresponding sulfur compound is light brown. The seleno-ether does not melt up to 300°.

Anal. Calcd.: Se, 18.19. Found: 18.49, 18.22.

Summary

The following new compounds have been prepared: 2,2-bis(seleno-ethyl)propane, $(CH_3)_2C(SeC_2H_5)_2$, 2,2-bis(seleno-ethyl)butane, $CH_3(C_2H_5)$-$C(SeC_2H_5)_2$, 3,3-bis(seleno-ethyl)pentane, $(C_2H_5)_2C(SeC_2H_5)_2$, ethyl seleninic acid hydronitrate, $C_2H_5SeO_2H{\cdot}HNO_3$, ethyl selenium tribromide, $C_2H_5SeBr_3$, bis(β-ethyl-selenomercapto-ethyl)sulfide, $(C_2H_5SeCH_2CH_2)_2S$, bis(β-ethyl-selenomercapto-ethyl)sulfoxide, $(C_2H_5SeCH_2CH_2)_2SO$, bis(β-ethyl-selenomercapto-ethyl)sulfone, $(C_2H_5SeCH_2CH_2)_2SO_2$, anthraquinone 1-butylsulfone-5-ethyl selenide, 1,5-$C_2H_5Se{\cdot}C_{14}H_6O_2{\cdot}SO_2C_4H_9$.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE INFLUENCE OF SULFUR ON THE COLOR OF AZO DYES. FURTHER INVESTIGATION

BY G. D. PALMER[1] AND E. EMMET REID

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In previous papers from this Laboratory,[2] the influence of sulfur in the *para* and *ortho* positions has been studied, and the position of the sulfur has been found to have marked influence. This suggested the investigation of the effect of sulfur in the *meta* position. In all three series, the four groups —CH_3, —OCH_3, —SCH_3 and —SO_2CH_3 have been contrasted. The first line of attack was to couple diazotized bases with *o*-cresol, guaiacol and *o*-methylmercaptophenol assuming that the coupling would take place *para* to the hydroxyl and hence *meta* to the other substituent, so that dyes would be obtained with the desired groups in the *meta* position. Diazotized sulfanilic acid did not couple satisfactorily with these phenols.[3] Naphthionic and gamma acids were diazotized and coupled with them and dyes were obtained, but the couplings did not appear to be complete and difficulties were encountered in proving the structure of the products. The bases *m*-$CH_3SC_6H_4NH_2$ and *m*-CH_3SO_2-$C_6H_4NH_2$, isomeric with those previously employed, have been prepared. These have been diazotized and coupled with R-salt, an intermediate that has been found to give satisfactory contrasts in the *ortho* and *para* series. For comparison, analogous dyes have been made from

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[1] From the Doctor's Dissertation of G. D. Palmer, **1924**.

[2] Waldron and Reid, THIS JOURNAL, **45**, 2399 (1923). Foster and Reid, *ibid.*, **46**, 1923 (1924).

[3] Zincke and Müller found difficulties in coupling with a similar compound. *Ber.*, **46,** 780 (1913).