Summary

Racemic adrenaline hydrochloride is readily converted into ethers in which the hydrogen of the secondary alcohol group is replaced by an alkyl group, by treating it with the corresponding absolute alcohol containing dry hydrogen chloride. The methyl and ethyl ethers have thus far been obtained and described. In the formation of the ethyl ether we have isolated as a by-product what appears to be di-adrenaline ether, formed by the condensation of 2 molecules of adrenaline with the elimination of 1 molecule of water from the 2 secondary alcohol groups.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM OXYCHLORIDE UPON ETHYLENE, PROPYLENE, BUTYLENE AND AMYLENE[1]

BY CARL E. FRICK

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Preliminary experiments by Lenher[2] have shown that the oxychloride of selenium reacts with saturated paraffin hydrocarbons only very slowly at high temperatures, while with the unsaturated hydrocarbons of the aliphatic series, it unites directly, frequently with great evolution of heat. Mueller[3] has reported that selenium oxychloride reacts with unsaturated hydrocarbons and ketones, producing substances that are very unstable in light and air. He gave no analytical results, however, nor any properties of the substances produced. The object of this investigation has been to make a quantitative study of the reactions taking place between selenium oxychloride and the olefins, ethylene, propylene, butylene and amylene; and to compare these reactions with those of selenium monochloride and the same olefins.

When selenium oxychloride reacts with ethylene, the dichloride of bis(β-chloro-ethyl)selenide is always produced, regardless of whether the ethylene or the oxychloride is in excess during the course of the reaction. With selenium monochloride and ethylene, Boord and Cope[4] have pointed out that this reaction takes place in two stages and that bis(β-chloro-ethyl)selenide is produced when the ethylene is in excess, while the dichloride of bis(β-chloro-ethyl)selenide is always formed when the monochloride is in excess.

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[1] This paper is constructed from a part of a thesis submitted by the author to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1923.

[2] Lenher, THIS JOURNAL, **43**, 29 (1921).

[3] Mueller, *Chem.-Ztg.*, **43**, 843 (1919).

[4] Boord and Cope, THIS JOURNAL, **44**, 395 (1922).

Preparation of Materials

Selenium Oxychloride.—The method of Lenher[5] was used, which consists in the union of selenium tetrachloride and selenium dioxide in a medium of carbon tetrachloride. The oxychloride was freed from carbon tetrachloride by fractionation and purified further by two distillations under reduced pressure.

The Olefins.—Ethylene and propylene were made by the method of Newth,[6] which consists in the dehydration of the corresponding alcohols with glacial phosphoric acid. *iso*Propyl alcohol was used in the preparation of the propylene. The best yields were obtained when the phosphoric acid was kept at a temperature of 210° in the case of the preparation of ethylene and at 360° in the case of the preparation of propylene. β-Butylene was prepared from *N*-butyl alcohol by the contact method of King.[7] The catalyst used was pumice stone impregnated with glacial phosphoric acid. Temperatures from 280–400° gave practically the same yields of β-butylene. The γ-butylene was removed by bubbling the gaseous product through 60% sulfuric acid. The amylene was a commercial sample and was purified by the method improved and successfully used in connection with the course in Organic Chemical Manufacturing at the University of Illinois.[8] This method worked very well and gave practically pure trimethylethylene, boiling at 36–38°. The yield was about 350 cc. per liter of crude amylene.

Experimental Part

In order to find out whether the same products were obtained in the interaction of selenium oxychloride and the olefins when the selenium oxychloride was added in excess, and when the olefin was in excess, two general procedures were used.

1. The olefin was passed into pure selenium oxychloride or a solution of it in an inert solvent, usually chloroform, until absorption of the olefin was completed. The reaction proceeded with evolution of heat and sometimes required cooling. When no more olefin was absorbed, the solvent was evaporated under diminished pressure, and the crude material was purified by crystallization from a suitable solvent. When a liquid product was obtained that could not be crystallized it was purified by fractional distillation under diminished pressure.

2. The selenium oxychloride in an inert solvent, usually chloroform, was dropped into an atmosphere of the olefin, in such a way that the latter was always maintained in excess throughout the course of the experiment. A 3-liter, Pyrex flask served as the reaction chamber and was fitted with a mercury-sealed glass stirrer, a dropping funnel, and an inlet and outlet tube for the olefin. The olefin was passed in until the air was displaced and the solvent saturated. The selenium oxychloride solution was then permitted to drop from the funnel at such a rate that the olefin was always maintained in excess. The reaction took place slowly, the walls of the flask becoming coated with selenium dioxide. After the

[5] Lenher, THIS JOURNAL, **42**, 2498 (1920).

[6] Newth, *J. Chem. Soc.*, **79**, 915 (1901).

[7] King, *ibid.*, **115**, 1401 (1919).

[8] Adams, Kamm and Marvel, "Organic Chemical Reagents," John Wiley and Sons. 1919.

addition of a measured quantity of the oxychloride solution, the agitation was continued for a few minutes in the presence of the olefin and the operation interrupted. The reaction mixture was filtered rapidly by suction and the solvent evaporated under reduced pressure. The crude, oily product was purified by crystallizations from a suitable solvent or by fractional distillation under diminished pressure, as the nature of the product required.

Bis(β-chloro-ethyl)selenide Dichloride.—(1) Dry ethylene was passed into a solution of 83 g. ($^1/_2$ mole) of selenium oxychloride dissolved in 200 cc. of anhydrous chloroform, until no more was absorbed. The ethylene was rapidly absorbed with evolution of heat, and a white, crystalline substance separated, clogging the inlet tube from time to time. The solution remained practically colorless; no reduction to selenium monochloride took place. (2) Two hundred cc. of a solution of selenium oxychloride in anhydrous chloroform, containing 85 g. of pure selenium oxychloride, was dropped slowly into an atmosphere of ethylene. A white, crystalline substance separated but more slowly than when the oxychloride was in excess.

The reaction mixtures were freed from the solvents by evaporation, the crude products purified by repeated crystallizations from chloroform or carbon tetrachloride, and dried at room temperature. Bis(β-chloro-ethyl)selenide dichloride was obtained in both cases, as long, white, prismatic crystals; m. p., 121.5°.

The product was analyzed for selenium by fusion of 0.2 g. of substance with 8–10 g. of a 1:1 mixture of anhydrous sodium carbonate and sodium peroxide. After fusion, the melt was dissolved with water, the solution acidified with hydrochloric acid and filtered. An excess of hydrochloric acid, sufficient to bring the concentration of the solution to 15 to 20% of hydrochloric acid, was added and the selenium precipitated from the hot solution by 25 cc. of a saturated solution of sulfur dioxide. Chlorine was determined either by fusion in a similar manner, acidifying with nitric acid and titrating by the Volhard method, or by Stepanoff's[9] absolute alcohol-sodium method.

Analyses. Calc. for $C_4H_8Cl_4Se$: C, 17.33; H, 2.91; Cl, 51.05; Se, 28.58. Found: C, 17.08, 16.97, 17.13; H, 2.91, 3.07, 3.30; Cl, 51.22, 51.49, 51.05; Se, 28.80, 28.45, 28.50.

When the crystals were dissolved in cold water it was found that partial hydrolysis had taken place. When a little nitric acid was added and the chlorine precipitated in the cold by silver nitrate, exactly $^1/_2$ of the total chlorine was precipitated.

Analysis. Total chlorine: 51.15. After hydrolysis in cold water only: 25.56.

This compound was first described by Heath and Semon,[10] who obtained it by passing ethylene into a solution of selenium monochloride. Their sample melted at 118°, and after they had made several analyses they came to the conclusion that it was symmetrical tetrachloro-diethyl selenide. About the same time, Bauser, Gibson and Pope,[11] making use of the same reaction, obtained a white, crystalline compound, slightly hygroscopic, melting at 122.5°. They showed by analysis that the compound was β-β'-dichloro-diethyl selenide dichloride, and that upon reducing this substance in water solution with sulfur dioxide, they obtained β-β'-dichloro-diethyl selenide as a colorless oil that solidified when cooled.

Because of this apparent disagreement in the results of these different workers, selenium monochloride was prepared by the method of Divers and Shimose,[12] and the reaction with ethylene duplicated. When ethylene was passed into the solution of

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[9] Stepanoff, This Journal, **38**, 711 (1916).

[10] Heath and Semon, *J. Ind. Eng. Chem.*, **12**, 1101 (1920).

[11] Bauser, Gibson and Pope, *J. Chem. Soc.*, **117**, 1453 (1920).

[12] Divers and Shimose, *ibid.*, **45**, 198 (1884).

selenium monochloride in benzene, red selenium separated and a white substance crystallized. After purification by crystallization from benzene, the product was shown by analysis as well as by its melting point to be identical with the product obtained from ethylene and selenium oxychloride, which has been shown to be bis(β-chloro-ethyl)-selenide dichloride.

Bis(β-chloropropyl)selenide Dichloride.—(1) Dry propylene gas was passed into a solution of 85 g. of pure selenium oxychloride until absorption was completed. The propylene was rapidly absorbed with evolution of heat. A white, crystalline substance separated at once. (2) A solution of about 40 g. of selenium oxychloride in 183 cc. of anhydrous chloroform was allowed to drop slowly into an atmosphere of propylene. A white, crystalline solid settled in this case also.

The reaction mixtures were freed from the solvents by evaporation, the solid products purified by repeated crystallizations from petroleum ether, and dried at room temperature. Bis(β-chloropropyl)selenide dichloride was obtained in both cases as white, plate-like crystals resembling naphthalene, melting at 80°.

Analyses. Calc. for $C_6H_{12}Cl_4Se$: C, 23.60; H, 3.96; Cl, 46.48; Se, 25.95. Found: C, 23.43; H, 3.98; Cl, 46.43; Se, 25.67.

This compound has been prepared by Boord and Cope[4] by passing propylene gas into an excess of selenium monochloride dissolved in benzene. They describe it as a white, crystalline compound melting at 81°.

Bis(β-chlorobutyl)selenide Dichloride.—In an attempt to isolate bis(β-chlorobutyl)-selenide dichloride, (1) dry β-butylene was passed into 85 g. of pure selenium oxychloride until absorption was completed. The butylene was rapidly absorbed with evolution of heat. A yellowish, viscous mass was obtained which was stable as long as the mixture was kept cooled in ice water. When the product was allowed to come to room temperature, red selenium separated and a dark, oily product remained. (2) A solution of 42 g. of selenium oxychloride in 183 cc. of anhydrous chloroform was dropped slowly into an atmosphere of β-butylene. A white, crystalline substance separated slowly (identified as selenium dioxide), and the solution became reddish-yellow. The chloroform was evaporated under reduced pressure and an oily substance remained. This crude product could not be induced to crystallize. It was decomposed by distillation even under strongly reduced pressure.

In several experiments, a small, dark red fraction was obtained, boiling at 104–108° under 68 mm. pressure.

Analyses. Calc. for $C_8H_{16}Cl_4Se$: Cl, 42.57; Se, 23.74. Calc. for $C_8H_{15}Cl_3Se$: Cl, 35.86; Se, 26.69. Found: Cl, 37.00, 37.08; Se, 26.70, 26.46.

The selenium content of this small fraction is near that required for the unsymmetrical β-β'-dichlorobutyl-β'-chlorobutyl selenide. It is improbable that this compound is one of the main products of the reaction; rather, it is present only in small amounts among the decomposition products. It is believed from observations made throughout the course of the reaction, that the dichloride of bis(β-chlorobutyl)selenide was formed whenever the temperature of the reaction mixture was kept below 10°. The formation of the same by-product, selenium dioxide, showed that the reaction proceeded in a manner similar to that of the reactions of ethylene and propylene with selenium oxychloride.

Boord and Cope[4] were also unable to obtain the dichloride of bis(β-chlorobutyl)-selenide when using selenium monochloride and butylene.

Bis(β-chloro-amyl)selenide Dichloride.—In an attempt to prepare bis(β-chloro-amyl)selenide dichloride, (1) 35 g. (0.5 mole) of amylene dissolved in 200 cc. of anhydrous chloroform was added gradually to 83 g. (0.5 mole) of selenium oxychloride dissolved in 200 cc. of anhydrous chloroform. As soon as the two solutions were brought together, selenium dioxide separated. After the reaction mixture had stood for 24 hours in a refrigerator, it was filtered and the chloroform evaporated under diminished pressure. (2) A solution of 83 g. (0.5 mole) of selenium oxychloride in one series of experiments, and 41.5 g. (0.25 mole) of selenium oxychloride in another series of experiments, each dissolved in 150 cc. of anhydrous chloroform, was allowed to drop slowly into 35 g. (0.5 mole) of amylene dissolved in 200 cc. of anhydrous chloroform and cooled to 0° in an ice-bath. Selenium dioxide separated at once, and after all of the selenium oxychloride solution had been added the selenium dioxide was separated and the chloroform evaporated under reduced pressure.

The crude products in each case did not crystallize, but underwent decomposition even under greatly reduced pressure. Selenium monochloride was identified as one of the liquid fractions, and there was obtained a small quantity of a pale yellow, almost colorless liquid; b. p., 85–100° (atm.). The product was doubtless a mixture of amyl chlorides. Pure tertiary amyl chloride boils at 86°.

Analyses. Calc. for $C_{10}H_{20}Cl_4Se$: Cl, 39.29; Se, 21.92. Calc. for $C_5H_{11}Cl$: Cl, 33.28. Found: Cl, 33.40, 33.19; Se, none.

It is believed that the reaction proceeded in a manner similar to that of ethylene and propylene with selenium oxychloride, and that the dichloride of bis(β-chloro-amyl)-selenide was formed whenever the reaction mixture was kept below 10°. Selenium dioxide was identified as a by-product.

Boord and Cope[4] were also unable to obtain the dichloride of bis(β-chloro-amyl)-selenide, when using selenium monochloride and amylene.

Discussion of Results

These results show clearly that when selenium oxychloride reacts with the olefin hydrocarbons, the dichlorides of the corresponding alkyl selenides, are always produced regardless of whether the olefin or the oxychloride are in excess during the course of the reaction. Selenium dioxide has been identified as the by-product in every case, and since no selenium monochloride or selenium is produced, the reaction may be expressed as follows: $2C_nH_{2n} + 2Cl_2SeO = (Cl\ C_nH_{2n})_2Se\ Cl_2 + SeO_2$.

It is interesting to compare the above equation with the one given by Boord and Cope[4] for the interaction of selenium monochloride and the oelfins when the selenium monochloride is in excess: $2\ C_nH_{2n} + 2\ Cl_2Se = Se = (ClC_nH_{2n})_2SeCl_2 + 3\ Se$. Boord and Cope give the mechanism of this latter reaction as evidence in favor of the unsymmetrical structure for selenium monochloride. The similarity of the two preceding equations as written, and the results obtained in the syntheses described in this paper, are offered as still further evidence of the correctness of the unsymmetrical formula for selenium monochloride. Boord and Cope have given the credit for the suggestion of this formula to Konek-Norwall[13] but it appears that Divers and Shimose,[14] nearly 30 years earlier, gave its formula as $Se = SeCl_2$, and to them, therefore, should be given the credit for suggesting this unsymmetrical structure.

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[13] Konek-Norwall, *Oesterr. Chem. Ztg.*, **16**, 288 (1913).

[14] Ref. 12, p. 194.

The author wishes to express his appreciation to Professor Victor Lenher, at whose suggestion and under whose direction this work was carried out.

Summary

1. The reactions between selenium oxychloride and ethylene, propylene, butylene and amylene have been studied.

2. The mechanism of the reaction between selenium oxychloride and the olefins has been formulated and has been compared with that of selenium monochloride and the olefins.

3. It has been shown that with selenium oxychloride and the olefins, the dichlorides of the corresponding alkyl selenides are always formed regardless of whether the oxychloride or the olefin is in excess during the course of the reaction.

4. It has been shown that the final reaction products of selenium monochloride and the olefins are identical with those formed by the interaction of selenium oxychloride and the olefins.

5. The results obtained in these syntheses have been offered as further evidence in favor of the unsymmetrical structure for selenium monochloride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM OXYCHLORIDE ON PURE RUBBER[1]

BY CARL E. FRICK

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In the studies on the oxychloride of selenium which have been in progress in this Laboratory, Lenher[2] has shown that pure rubber, vulcanized rubber and vulcanite react chemically with selenium oxychloride. It seemed advisable to undertake a quantitative study of this reaction, if possible, as any information would be interesting in view of our incomplete knowledge of the nature of the rubber hydrocarbon. The products obtained by the action of selenium oxychloride on 2 wild, and 2 plantation rubbers, and a synthetic rubber prepared from isoprene, were investigated.

Preparation of Materials

Selenium Oxychloride.—The method of Lenher[3] was used.

Pure Rubber Hydrocarbon.—Samples[4] of crude, unworked rubber were washed

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[1] This paper is constructed from a part of a thesis submitted by the author to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1923.

[2] Lenher, THIS JOURNAL, **43**, 29 (1921).

[3] Lenher, *ibid.*, **42**, 2498 (1920).

[4] These samples were kindly furnished by Dr. W. C. Geer of the B. F. Goodrich Co. and Prof. H. E. Simmons of the University of Akron.