

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

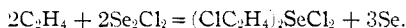
**THE ACTION OF SELENIUM MONOCHLORIDE UPON PROPYLENE, BUTYLENE AND AMYLENE.<sup>1</sup>**

BY C. E. BOORD AND F. F. COPE.

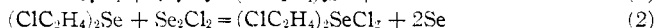
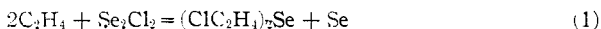
Received November 25, 1921.

Recent publications by Heath and Semon<sup>2</sup> and by Bauser, Gibson and Pope<sup>3</sup> make it desirable to publish an extension of work previously done in this laboratory.<sup>4</sup>

By passing ethylene into a solution of selenium monochloride, Heath and Semon obtained a white crystalline compound melting at 118°, which they have described as symmetrical tetrachloro-diethyl selenide. Bauser, Gibson and Pope by the same reaction obtained the crystalline compound melting at 122°, and have described it as  $\beta, \beta'$ -dichloro-diethyl selenide dichloride. Upon reducing this substance in water solution with sulfur dioxide they obtained  $\beta, \beta'$ -dichloro-diethyl selenide as a colorless oil which solidified when cooled. Basing their conclusions upon the nature of the products formed and upon the amount of selenium recovered these authors have represented the absorption of ethylene as follows.



Upon extending this reaction to the higher olefins, we have been able to show that the equation given above is the summation of two perfectly definite but consecutive reactions.



By passing the olefin into the selenium monochloride as the workers mentioned above have done, the ideal conditions for completing both stages are obtained. The action may be stopped at the end of the first stage by the simple process of reversing the order of bringing together the reagents.

**Preparation of Materials.**

**Selenium Monochloride.**—The method described by Divers and Shimose<sup>5</sup> and used in a modified form both by Heath and Semon<sup>2</sup> and by Bauser, Gibson and Pope<sup>3</sup> is suitable for obtaining pure selenium monochloride. In this work the monochloride was always used in solution, so a more direct method was employed. Evans and Ramsay<sup>6</sup> have pointed out that selenium rapidly absorbs chlorine. This suggests the preparation of the chlorides of selenium by a method quite analogous to that used for the preparation of the chlorides of sulfur.

<sup>1</sup> Read before the Organic Section of the American Chemical Society at New York City, September 8, 1921. See *Science*, **54**, 526 (1921).

<sup>2</sup> Heath and Semon, *J. Ind. Eng. Chem.*, **12**, 1101 (1920).

<sup>3</sup> Bauser, Gibson and Pope, *J. Chem. Soc.*, **117**, 1453 (1920).

<sup>4</sup> Burrell, *J. Ind. Eng. Chem.*, **11**, 101 (1919).

<sup>5</sup> Divers and Shimose, *J. Chem. Soc.*, **45**, 198 (1884).

<sup>6</sup> Evans and Ramsay, *ibid.*, **45**, 62 (1884).

In our earlier work the procedure used was as follows. A weighed quantity of finely divided metallic selenium was placed in a large round-bottom flask which had been provided with inlet and outlet tubes. A rapid current of dry chlorine was led in, close to the surface of the selenium. The absorption of chlorine was very rapid even at room temperature. The reaction took place with much heat evolution and the mixture became first pasty, then fluid and finally quite mobile. The rate of chlorination and the stirring were so adjusted as to avoid the formation of the yellowish-white incrustation of selenium tetrachloride on the walls of the flask and surface of the reaction mixture in so far as possible. Chlorination was stopped somewhat short of the gain in weight required to convert the selenium completely into the monochloride. The reaction mixture was now diluted with an indifferent solvent such as chloroform, carbon tetrachloride or benzene, filtered from undissolved selenium, and the solution of selenium chlorides thus obtained used for the interaction with the olefin.

In our later experiments the metallic selenium was suspended in one of the solvents mentioned above (benzene being used only after it had been shown that no appreciable amount of the chlorination products of benzene were formed) and chlorine led in with rapid stirring. In a typical run 200 g. of selenium was placed in a 1-liter flask and covered with 800 cc. of benzene. Chlorine was passed in rapidly until 89.46 g. (1 atom equivalent) had been absorbed. The absorption took place with the evolution of heat and almost no chlorine escaped from the reaction chamber. Filtration left a little unchanged selenium.

By neglecting the small amount of selenium dissolved unchanged one may calculate, from the weights of selenium used and recovered and weight of chlorine absorbed, the approximate amounts of selenium mono- and tetra-chloride formed. That such an approximation is justified is shown by the results obtained in the condensations described below.

**Olefins.**—Propylene, butylene and amylene were prepared from the corresponding monohydric alcohols by the contact process. The alcohol was admitted dropwise into the vertical arm of an iron tube 38 mm. in diameter and 120 cm. long mounted on a 21-burner combustion furnace. Anhydrous aluminum sulfate was used as the catalyst. In the preparation of amylene, amyl alcohol was passed through the tube at a temperature of 335°. The amylene was condensed, separated from the water, dried, and fractionated. The major portion boiled at 40–41°. Butylene was prepared from *N*-butyl alcohol at a temperature of 340° and had a purity of 92–95% by the bromine method. Propylene was prepared from *isopropyl* alcohol at a temperature of 360° with a purity of 90 to 91%.

### Experimental Part.

The logical condition for the direct preparation of *bis*( $\beta$ -chloro-alkyl) selenide is to bring the selenium monochloride into reaction with the olefin in such a way that the latter will be always in excess. This was accomplished by spraying the monochloride solution into an atmosphere of the olefin. The following general procedure was used.

A 2-liter, 3-necked Pyrex flask served as the reaction chamber. The large middle neck was provided with a 2-hole stopper bearing a stirring paddle and a dropping funnel. The stirring paddle was provided with a mercury seal and 2 sets of vanes, one for agitating the reaction mixture and one passing just below the tip of the dropping funnel for spraying the monochloride solution. Through one side-neck passed an inlet for the olefin and on the second was mounted a reflux condenser

To start the reaction, 200 cc. of anhydrous benzene was placed in the reaction chamber and violently agitated by mechanical stirring. The olefin was led in until the air was displaced and the solvent saturated. Selenium monochloride solution in benzene was now permitted to flow drop-wise from the dropping funnel onto the rapidly moving spray paddles at such a rate that the olefin could always be maintained in excess. The reaction was instantaneous, the walls of the flask becoming coated with amorphous selenium. After the addition of a measured quantity of the monochloride 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 deposited selenium washed with anhydrous benzene, collected, dried and weighed. The filtrate was evaporated and the oily crude product purified by distillation under diminished pressure.

The general procedure for the direct preparation of *bis*( $\beta$ -chloro-alkyl) selenide dichlorides was much simpler. Here, it was sufficient that the olefin be led into the selenium monochloride solution until one mol had been absorbed. The reaction proceeded with heat evolution and sometimes required cooling. When the reaction was completed, the mixture was filtered warm and the deposited selenium washed repeatedly with warm benzene, dried and weighed. The combined filtrate and washings were evaporated to crystallization or to constant weight as the nature of the product required.

With the simpler olefins the second step in the reaction goes quite rapidly but with butylene and amylene it goes more slowly so that a longer time is required for the reaction to be completed.

***Bis*( $\beta$ -chloropropyl) Selenide.**—Three hundred cc. of a solution of selenium monochloride in benzene, containing 93 g. of selenium monochloride (64.2 g. of selenium) was led drop-wise into an atmosphere of propylene. Thirty-two g. or  $1/2$  of the selenium was recovered as free selenium. The oily crude product obtained upon evaporation of the filtrate was purified by distillation under diminished pressure. *Bis*( $\beta$ -chloropropyl) selenide was obtained as a lemon-yellow oil boiling at  $134^\circ$  under 10 mm. pressure.

The product was analyzed by digesting the sample with 20 cc. of 10% sodium hydroxide solution for 30 minutes, acidifying with nitric acid and titrating by the Volhard method.

*Analyses.* Calc. for  $C_6H_{12}Cl_2Se$ : Cl, 30.26. Found: 30.33, 30.24.

***Bis*( $\beta$ -chloropropyl) Selenide Dichloride.**—Dry propylene gas was led into a solution of 93 g. of selenium monochloride (64.2 g. of selenium) in anhydrous benzene until one mol had been absorbed. The propylene was rapidly absorbed with heat evolution. The reaction mixture was allowed to stand for 24 hours in order that the second stage of the reaction might have ample time to be completed.

Theoretically, 48.15 g. or  $3/4$  of the selenium should be deposited in the two consecutive stages of the reaction; 45.5 g. was actually recovered. Upon evaporation of the filtrate a white crystalline product separated. The crude product was recrystallized from chloroform and dried at room temperature. *Bis*( $\beta$ -chloropropyl) selenide dichloride was obtained as white crystals melting at  $81^\circ$ .

*Analysis.* Calc. for  $C_6H_{12}Cl_4Se$ : Cl, 46.46. Found: 45.97.

*Bis*( $\beta$ -chlorobutyl) Selenide was prepared by spraying a benzene solution of selenium monochloride into an atmosphere of butylene. Two hundred and fifteen cc. of selenium monochloride solution containing 68 g. of the monochloride (47 g. of selenium) was used, and 22.5 g. (calc. 23.5 g.) of selenium was recovered. The crude product obtained by evaporation of the solvent was submitted to distillation under reduced pressure. *Bis*( $\beta$ -chlorobutyl) selenide was obtained as a yellow oil boiling at  $138^\circ$  under 8 mm. pressure. The product slowly darkens upon exposure to light.

*Analyses.* Calc. for  $C_8H_{16}Cl_2Se$ : Cl, 27.02. Found: 27.25, 27.29.

*Bis*( $\beta$ -chlorobutyl) Selenide Dichloride.—In an attempt to prepare *bis* ( $\beta$ -chlorobutyl) selenide dichloride, 200 cc. of a benzene solution containing 64 g. of selenium monochloride (44 g. of selenium) was permitted to absorb an equimolecular quantity of dry butylene. The reaction mixture was allowed to stand for 24 hours and was then filtered. Instead of the calculated 33 g. ( $3/4$ ) only 26.5 g. of selenium was recovered as free selenium. The oily, crude product obtained upon evaporating the filtrate could not be induced to crystallize. It was decomposed by distillation even under strongly reduced pressure. After driving off the benzene as completely as possible, the crude product analyzed with the following results.

*Analyses.* Calc. for  $C_8H_{16}Cl_4Se$ : Cl, 42.57; calc. for  $C_8H_{16}Cl_2Se$ : Cl, 27.02. Found: 36.41, 36.64.

Both the chlorine content and the amount of selenium recovered indicate that the second stage of the reaction did not go to completion.

A solution of 15 g. of selenium monochloride (10.4 g. of selenium) in benzene was treated with an equimolecular quantity of *bis*( $\beta$ -chlorobutyl) selenide. The reaction began immediately with the deposition of selenium. After standing for 24 hours at room temperature, the reaction mixture was filtered, whereupon 7 g. (calc. 10.4 g.) of selenium was recovered.

The chlorine content of the crude product is near that required for the unsymmetrical trichloro derivative,  $\beta, \beta$ -dichloro-butyl- $\beta'$ -chlorobutyl selenide. That this product is not present in quantity, however, is evidenced by the fact that when the crude product is reduced in water solution with sulfur dioxide and the resulting oil dried and purified it distills at  $138^\circ$  under 8 mm. pressure, shows by analysis a chlorine content of 26.82% and is thus identical with *bis*( $\beta$ -chlorobutyl) selenide.

*Bis*( $\beta$ -chloro-amy) Selenide.—Since amyene is a liquid at room temperature, the operation in this case becomes quite simple. Thirty-five g. ( $1/2$  mol) of amyene was dissolved in 200 cc. of anhydrous benzene in the reaction chamber. A solution of 57.5 g. ( $1/4$  mol) of selenium monochloride in anhydrous benzene was added drop-wise with stirring. When the reaction was complete, the selenium was filtered off, washed with benzene and weighed. Of the 39.6 g. of selenium used, 19.5 g. was recovered as free selenium. The crude product obtained by evaporating the solvent was submitted to fractionation under diminished pressure. *Bis*( $\beta$ -chloro-amy) selenide was obtained as a reddish-yellow oil boiling at  $158^\circ$  under 10 mm. pressure. The product cannot be completely distilled even under 10 mm. pressure with partial decomposition.

*Analyses.* Calc. for  $C_{10}H_{20}Cl_2Se$ : Cl, 24.41. Found: 23.92, 24.43.

*Bis*( $\beta$ -chloro-amy) Selenide Dichloride.—In an attempt to prepare *bis*( $\beta$ -chloro-amy) selenide dichloride, 35 g. ( $1/2$  mol) of amyene was gradually added to 115 g. ( $1/2$  mol) of selenium monochloride with stirring. Free selenium was deposited immediately. After standing for 24 hours, the reaction mixture was filtered, and 48 g. (calc. 59.7 g.) or  $3/4$  of the selenium was recovered. The chlorine content of the crude oil lay between that of the selenide and its dichloride.

*Analyses.* Calc. for  $C_{10}H_{20}Cl_2Se$ : Cl, 24.41; calc. for  $C_{10}H_{20}Cl_4Se$ : Cl, 39.27. Found: Cl, 29.44, 29.79.

By fractional distillation under diminished pressure there was obtained a quantity of reddish-yellow oil boiling at  $158^\circ$  under 10 mm. pressure. This product is doubtless unchanged *bis*( $\beta$ -chloro-amy) selenide.

*Analyses.* Calc. for  $C_{10}H_{20}Cl_2Se$ : Cl, 24.41. Found: 24.97, 24.85.

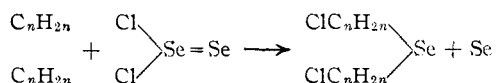
A solution of 15 g. of selenium monochloride in benzene was treated with a benzene solution of *bis*( $\beta$ -chloro-amy) selenide in equimolecular quantities. Of the theoretical 10.4 g. of free selenium, 6 g. was recovered.

### Discussion of Results.

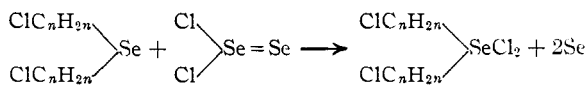
The above results demonstrate beyond question that the relation between the two products described for a given olefin is the same as that of alkyl selenide and corresponding alkyl selenide dichloride. The equation used to explain the mechanism of their formation will depend upon the structure accepted for selenium monochloride. The structure most adaptable is that suggested by Konek-Norwall<sup>7</sup> which represents it as unsymmetrical di-

chloro-diselenide  $\begin{matrix} Cl \\ \diagdown \\ \diagup \\ Cl \end{matrix} Se = Se$ . In fact, the authors believe the results obtained in the syntheses described above to be strong evidence of the correctness of the unsymmetrical structure of selenium monochloride.

Using the unsymmetrical structure for selenium monochloride, the absorption of olefins may be expressed as follows.

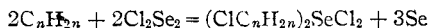


This is the first stage of the reaction and represents what takes place when selenium monochloride is brought into an excess of the olefin. The conversion of alkyl selenides into their dichlorides by direct chlorination or by further reaction with active chlorides is a well-known reaction.<sup>8</sup> This accounts for the second stage of the reaction which takes place when the olefin is led directly into selenium monochloride solution.



The simple selenide first formed is converted by the excess of selenium monochloride into the selenide dichloride, setting free 2 additional atoms of selenium.

The summation of these two equations is analogous to that given by Pope and his co-workers.<sup>3</sup>

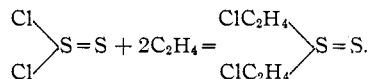


<sup>7</sup> Konek-Norwall, *Oesterr. Chem. Zig.*, **16**, 288 (1913).

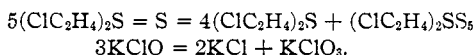
<sup>8</sup> Joy, *Ann.*, **86**, 35 (1853). Jackson, *ibid.*, **179**, 1 (1875).

### The Chemistry of the Formation of Mustard Gas.

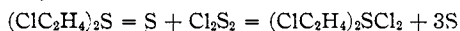
The chemistry involved in the preparation and properties of the selenium derivatives is of interest, further, in the light it sheds upon the formation of the mustard gas from sulfur monochloride. Accepting an analogous structure for sulfur monochloride the absorption of ethylene may be expressed



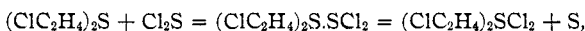
In this case the persulfide sulfur atom being more like chlorine does not always split off spontaneously. This structure, which has already been suggested by Green,<sup>9</sup> readily accounts for the formation of mustard gas polysulfides, the existence of which has been so clearly demonstrated by Conant, Hartshorn and Richardson.<sup>10</sup> The mechanism of this polysulfide formation is probably quite analogous to that by which hypochlorites are converted into chlorates.



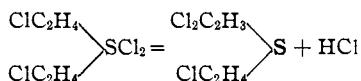
The tendency of sulfur and selenium to seek a higher valence when in the form of their alkyl derivatives may also be an explanation of the fact observed by Conant, Hartshorn and Richardson that the chlorides of sulfur, particularly the dichlorides, rapidly absorb only one molecular quantity of ethylene, when ethylene is led into the sulfur chloride solution.



or



the hypothetical mustard gas dichloride undergoing spontaneous decomposition with the evolution of hydrogen chloride and the simultaneous formation of the trichloro derivative.



In this connection it is interesting to note the observations of Williams,<sup>11</sup> who says: "It is essential that the reaction between ethylene and sulfur monochloride be completed in the minimum possible time;" and also of Gibson and Pope,<sup>12</sup> who state: "The sulfur dichloride method is difficult to control, because  $\beta, \beta'$ -dichloro-ethyl sulfide is acted on rapidly by sulfur dichloride; it is necessary that little or no sulfur dichloride remain long in contact with the  $\beta, \beta'$ -dichloro-ethyl sulfide produced." Meyers<sup>13</sup> has

<sup>9</sup> Green, *J. Soc. Chem. Ind.*, **38**, 469R (1919).

<sup>10</sup> Conant, Hartshorn and Richardson, *THIS JOURNAL*, **42**, 585 (1920).

<sup>11</sup> Williams, *J. Soc. Chem. Ind.*, **38**, 451R (1919).

<sup>12</sup> Gibson and Pope, *J. Chem. Soc.*, **117**, 271 (1920).

<sup>13</sup> Meyers, *J. Soc. Chem. Ind.*, **39**, 65T (1920).

reported that by spraying sulfur dichloride into an atmosphere of ethylene he was able to obtain mustard gas of 93% purity after one distillation.

### Summary.

1. The reaction between selenium monochloride and olefins is shown to take place in two stages.

2. By spraying the monochloride or its solution into an atmosphere of olefin the reaction may be stopped at the first stage. In this manner *bis*-( $\beta$ -chloropropyl) selenide, *bis*-( $\beta$ -chlorobutyl) selenide, and *bis*-( $\beta$ -chloro-amy) selenide have been prepared, and their properties described.

3. By leading the olefin into selenium monochloride or its solution the above products are acted upon by the excess of the monochloride, being converted into *bis*-( $\beta$ -chloropropyl) selenide dichloride, *bis*-( $\beta$ -chlorobutyl) selenide and *bis*-( $\beta$ -chloro-amy) selenide dichloride, respectively. This constitutes the second stage of the reaction.

4. The mechanism of the reaction between selenium monochloride and olefins is formulated, using the unsymmetrical structure for selenium monochloride. The quantitative results obtained in these syntheses is offered as evidence in favor of the unsymmetrical structure for selenium monochloride.

5. The same mechanism has been applied to explain the formation of mustard gas from ethylene and sulfur monochloride. The possibility of preparing mustard gas by spraying sulfur monochloride is again pointed out.

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## CRYSTALLINE CHLORO-TETRA-ACETYL MANNOSE.

BY D. H. BRAUNS.

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A halogenated derivative of an acetylated sugar was first obtained by Colley<sup>1</sup> by the action of acetyl chloride on glucose in a sealed tube at room temperature. The author, however, succeeded only twice in crystallizing the syrupy chloro-tetra-acetyl glucose. As this derivative was found to be a valuable intermediate for preparing synthetic glucosides,<sup>2</sup> many chemists have studied different methods for preparing crystalline halogenated acetyl derivatives of sugars. Koenigs and Knorr<sup>3</sup> prepared bromo-acetyl glucose in a crystalline condition by shaking glucose with acetyl bromide at ordinary temperature, the derivative separating from the

<sup>1</sup> Colley, *Ann. chim. phys.*, [4] 21, 367 (1870).

<sup>2</sup> Michael, *Am. Chem. J.*, 1, 305 (1879).

<sup>3</sup> Koenigs and Knorr, *Ber.*, 34, 957 (1901).