CCLIII.—*ββ'-Dichloro- and ββ'-Dibromo-diethyl Selenides and their Simple Halogen Derivatives.*

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IN studying the reaction between ethylene and selenium monochloride, Bausor, Gibson, and Pope (J., 1920, **117**, 1453) showed that ββ'-dichlorodiethyl selenide dichloride (m. p. 122·5°) is formed and that the reaction proceeds according to the equation $2CH_2{:}CH_2 + 2Se_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2SeCl_2 + 3Se$. Heath and Semon (*Ind. Eng. Chem.*, 1920, **12**, 1100) suggested that the final product is *s*-tetrachlorodiethyl selenide, $(CHCl_2{\cdot}CH_2)_2Se$, m. p. 118°.† On the other hand, Boord and Cope (*J. Amer. Chem. Soc.*, 1922, **44**, 395) agree that the final product is ββ'-dichlorodiethyl selenide dichloride, but they advance arguments to prove that the reaction goes in two stages:

$$(a)\ 2C_2H_4 + Se_2Cl_2 = (C_2H_4Cl)_2Se + Se.$$
$$(b)\ (C_2H_4Cl)_2Se + Se_2Cl_2 = (C_2H_4Cl)_2SeCl_2 + 2Se.$$

In their paper Boord and Cope do not give any indication that they have investigated the reaction between ethylene and selenium

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† These authors state that hydrogen chloride is evolved during the reaction. We have found that this is not so if precautions are taken to exclude moisture.

monochloride and did not isolate ββ′-dichlorodiethyl selenide which, the present work has further proved, was described by Bausor, Gibson, and Pope for the first time (compare Boord, *Ind. Eng. Chem.*, 1919, **11**, 101). The argument advanced by Boord and Cope is based on the results of experiments on the reaction between selenium monochloride and propylene, butylene, and amylene, respectively, and they show in each case that when selenium monochloride is added to the olefine the ββ′-dichlorodialkyl selenide is produced (reaction *a*). The only case of the formation of a selenide dichloride found by Boord and Cope was when they carried out the reaction between selenium monochloride and propylene, substantially under the conditions maintained by Bausor, Gibson, and Pope in the case of ethylene, and they obtained ββ′-dichlorodipropyl selenide dichloride. If the reaction between the olefines and selenium monochloride is a general one and occurs in two stages as stated by Boord and Cope, then that between the selenide and selenium monochloride (*b*) must be quantitative and proceed under the ordinary conditions of the experiment. In only one case apparently did the authors try this; they found that when equimolecular quantities of selenium monochloride and ββ′-dichlorodibutyl selenide were mixed the selenide dichloride was not obtained. The work of Boord and Cope indicates that the selenide dichlorides from butylene and amylene are difficult to prepare and may not have been obtained, but it affords little evidence that the reaction between ethylene and selenium monochloride takes place in two stages.

When selenium monochloride in chloroform is added to a chloroform solution of ββ′-dichlorodiethyl selenide at the ordinary temperature the formation of ββ′-dichlorodiethyl selenide dichloride is, we find, instantaneous and selenium separates at once. Although it may be convenient to regard the formation of the selenide as a phase in the reaction, it is clear that it cannot exist in the presence of selenium monochloride for any appreciable time. We describe below a highly satisfactory method for the preparation of ββ′-dichlorodiethyl selenide from the dichloride in which the possibility of its contamination with selenium is avoided and since the preparation of the dichloride can be carried out so readily we have not investigated the possibility of the preparation of the somewhat toxic selenide directly from selenium monochloride which, at the best, would involve the separation of the product from selenium.

ββ′-Dichlorodiethyl selenide dichloride can be prepared not only by the action of ethylene on selenium monochloride, but also in quantitative yield from selenium tetrachloride,

$$2C_2H_4+SeCl_4=(CH_2Cl\cdot CH_2)_2SeCl_2,$$

and the separation of the product from selenium is thereby avoided. It is possible to chlorinate selenium in the presence of benzene (very little chlorination of the latter takes place) or other suitable solvents to the tetrachloride and to convert this quantitatively into the final product, the same vessel being used throughout. In an analogous manner, ββ′-*dibromodiethyl selenide dibromide* is obtained, starting with selenium.

Bausor, Gibson, and Pope suggested that the colourless, crystalline substance, m. p. 23—25°, obtained in small quantity by reducing a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride with sulphur dioxide is probably ββ′-dichlorodiethyl selenide (*loc. cit.*). This is the fact. It can also be prepared by reducing the dichloride with hydrogen sulphide or, best, with potassium metabisulphite. It has a characteristic and persistent garlic-like odour and its toxicity appears to be very much less than that of ββ′-dichlorodiethyl sulphide. The corresponding ββ′-*dibromodiethyl selenide* is prepared in an analogous manner by reduction of the corresponding dibromide.

On treatment under appropriate conditions with either chlorine or bromine, the selenides combine with two atomic props. of the halogen. Apart from the dichloride and the dibromide already mentioned, we have prepared in this way ββ′-*dichlorodiethyl selenide dibromide* and ββ′-*dibromodiethyl selenide dichloride*. Since chlorine combines with ββ′-dichlorodiethyl selenide to give the product obtained by the reaction of ethylene with selenium monochloride, these compounds afford additional evidence of the correctness of the constitution given to ββ′-dichlorodiethyl selenide dichloride by Bausor, Gibson, and Pope. ββ′-Dichlorodiethyl selenide dichloride is precipitated from its aqueous solution by hydrochloric acid, and similarly the corresponding dibromide is precipitated by hydrobromic acid. The product obtained by adding hydrochloric acid to an aqueous solution of ββ′-dibromodiethyl selenide dibromide was proved to be the dichloride by its yielding ββ′-dibromodiethyl selenide on reduction with potassium metabisulphite. Under similar conditions, ββ′-dichlorodiethyl selenide dibromide is converted into ββ′-dichlorodiethyl selenide. It is interesting to compare the instability of ββ′-dichlorodiethyl sulphide dibromide (Gibson and Pope, J., 1920, **117**, 277) with the great stability of the analogous compounds of selenium now described.*

* Propylene reacts with selenium tetrachloride in a precisely similar manner to ethylene, and a quantitative yield of *ββ′*-dichlorodipropyl selenide dichloride results. This compound, reduced by potassium metabisulphite, is converted quantitatively into *ββ′*-dichlorodipropyl selenide (compare Boord and Cope, *loc. cit.*).

So far, all attempts to prepare direct oxidation products of ββ′-dichlorodiethyl selenide have failed. Although part of it is destroyed in the process, ββ′-dichlorodiethyl selenide dichloride can be recrystallised from concentrated nitric acid. Under the conditions for converting ββ′-dichlorodiethyl sulphide into the corresponding sulphoxide (Gibson and Pope, *loc. cit.*), ββ′-dichlorodiethyl selenide is partly destroyed and the dichloride crystallises out from the solution. Although the dichloride in aqueous solution behaves like the chloride of a bivalent metal, we have not been able to isolate either the corresponding hydroxide or oxide. An attempt to prepare the oxide by the action of ethylene on selenium oxychloride resulted in the formation of the dichloride and selenium dioxide, the following reaction presumably taking place :

$$2SeOCl_2+2C_2H_4=SeO_2+(C_2H_4Cl)_2SeCl_2.$$

EXPERIMENTAL.

ββ′-Dichlorodiethyl Selenide Dichloride.—Some quantity of this compound was prepared by the original method from selenium monochloride and the previous results were confirmed in all respects. When an excess of dry ethylene was passed into a dry benzene solution of selenium monochloride, hydrogen chloride was not evolved for the issuing gas produced no change in the alkalinity of standard sodium hydroxide. In an actual experiment, dry ethylene was passed into a rapidly stirred solution of 42 g. of selenium monochloride in dry benzene, cooled in running water. The yields of ββ′-dichlorodiethyl selenide dichloride and of precipitated selenium obtained were 24 g. and 19 g., respectively; according to the equation, they should be 25·4 g. and 21·7 g.

The preparation from selenium tetrachloride is, however, much more convenient, since all contamination with selenium is avoided. A rapid stream of chlorine is passed into a cooled, well-stirred suspension of finely divided selenium (1 part) in a convenient amount of benzene (carbon tetrachloride, chloroform or ether may be used). Selenium tetrachloride is formed with evolution of heat and separates rapidly as a pale yellow powder. The chlorine supply is then cut off, finely divided selenium (3 parts) added, and stirring continued for some time, during which the selenium tetrachloride is converted into the monochloride and almost complete solution is effected. The somewhat diluted benzene solution is filtered in a dry atmosphere, and chlorination is continued rapidly under the same conditions as before until the solution is completely decolorised and the selenium tetrachloride separates as a pale yellow powder, almost insoluble in most organic solvents. After freeing the solution from excess of chlorine by passing dry air, ethylene is passed in until complete solution of the selenium tetrachloride is effected in the warm solvent, which should become quite colourless when the reaction is finished. The dichloride crystallises as the solution cools and the small amount remaining in solution can be recovered in the usual manner. In this way, from a total amount of 20 g. of selenium, 60—65 g. of ββ′-dichlorodiethyl selenide dichloride can be prepared conveniently in the course of about 8 hours including the preparation of the necessary ethylene. That the reaction between selenium tetrachloride and ethylene takes place according to the equation $2C_2H_4+SeCl_4=(C_2H_4Cl)_2SeCl_2$ was proved by passing ethylene into dry benzene in which 10 g. of the tetrachloride was suspended. Twelve grams of the resulting compound was obtained (theory requires 12·5 g.).

The identity of the compound prepared from selenium tetrachloride with that prepared from the monochloride was proved by its melting point (122·5°), by its crystalline form, and by its behaviour with sodium hydroxide in cold aqueous solution (Found : titratable Cl, 25·9; *M*, cryoscopic in hexachloroethane,* 276. Calc. for $C_4H_8Cl_4Se$: titratable Cl, 25·6%; *M*, 277·2). The compound is best purified by recrystallisation from chloroform. It can be almost quantitatively recovered from its aqueous solution by addition of concentrated hydrochloric acid and this is also a convenient method of purification. Its aqueous solution decomposes above 35°, and rapidly when boiled, with evolution of ethylene.

When concentrated hydrobromic acid was added to a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride, a yellow, crystalline precipitate was obtained which, after recrystallisation from chloroform, had m. p. 117° (decomp.) and was proved by its constants and by analysis to be *ββ′-dichlorodiethyl selenide dibromide*, obtained also in another way (see p. 1883).

In attempts to isolate ββ′-dichlorodiethyl selenide dihydroxide, careful addition of sodium hydroxide (2 equivs.) to the aqueous solution of the dichloride gave negative results. Similarly, in attempting to prepare ββ′-dichlorodiethyl selenide oxide by the action of dry silver oxide on a benzene solution of the dichloride, selenium was deposited and no oxide-like substance could be isolated.

ββ′-Dibromodiethyl Selenide Dibromide, $(CH_2Br{\cdot}CH_2)_2SeBr_2$, is prepared in an analogous manner to the dichloride. Finely divided selenium is suspended in pure carbon tetrachloride and bromine is added to the rapidly stirred suspension until the whole of the

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* The use of hexachloroethane for the determination of molecular weights has not yet been described but, as soon as its general applicability has been determined, an account will be submitted for publication.

bromine is converted into the tetrabromide. The excess of bromine is removed either by boiling or by passing a current of dry air. Dry ethylene is then passed into the rapidly stirred suspension of the tetrabromide until the solution becomes clear; the ββ'-dibromodiethyl selenide dibromide dissolves in the warm solvent and crystallises on cooling. One crystallisation from chloroform is sufficient for complete purification, well-formed, bright yellow prisms, m. p. 118°, being obtained (Found: Br, 71·1. $C_4H_8Br_4Se$ requires Br, 71·6%).

ββ'-*Dichlorodiethyl Selenide*, $(CH_2Cl\cdot CH_2)_2Se$.—The substance, m. p. 23—25°, originally prepared by Bausor, Gibson, and Pope (*loc. cit.*) by passing sulphur dioxide into a cold aqueous solution of ββ'-dichlorodiethyl selenide dichloride, was prepared again by the same method and proved to be ββ'-dichlorodiethyl selenide identical with the product obtained more conveniently by a slightly different procedure.

ββ'-Dichlorodiethyl selenide dichloride may be reduced in boiling benzene solution by dry hydrogen sulphide. Sulphur separates and the reaction is finished when hydrogen chloride ceases to be evolved. On distilling off the benzene from the filtered solution, a product is obtained, m. p. about 24°, which is extremely difficult to obtain free from adhering sulphur. On extraction with dry ether, some sulphur is left undissolved, but the melting point of the product is scarcely affected. Fractional freezing of the material to free it from sulphur is not very satisfactory and even after repeating this process several times analysis shows that the resulting material is not quite pure (Found: Cl, 33·2%).

After many experiments the following method was finally adopted for preparing ββ'-dichlorodiethyl selenide conveniently in a state of purity. A solution of pure ββ'-dichlorodiethyl selenide dichloride (10—15 g.) in cold water is shaken with cold aqueous potassium metabisulphite (calc. quantity) and at once extracted with ether. The ethereal solution is washed with water, dried with calcium chloride, and evaporated; the selenide crystallises easily (yield almost theoretical). It is convenient to purify it by pressing on to clean unglazed porcelain and subsequent fractional freezing. It crystallises in colourless needles, m. p. 24·2° (Found: Cl, 34·7; Se, 38·6; *M*, cryoscopic in benzene, 196. Calc. for $C_4H_8Cl_2Se$: Cl, 34·4; Se, 38·4%: *M*, 206). Unlike the corresponding sulphide, it cannot be distilled in a water-pump vacuum without considerable decomposition. The distillate, however, contains some unchanged selenide which is identified by conversion into the dibromide (see below).

ββ'-Dichlorodiethyl selenide combines with chlorine (1 mol.) to give the dichloride and with bromine (1 mol.) in chloroform solution. The reaction is quantitative: 0·3915 g. decolorised 0·315 g. bromine, the theoretical quantity being 0·303 g. bromine. The compound so formed is therefore ββ'-*dichlorodiethyl selenide dibromide*, $(C_2H_4Cl)_2SeBr_2$, which crystallises from chloroform in pale yellow prisms, m. p. 117° (decomp.). This compound, on reduction with potassium metabisulphite in the manner already described, yields ββ'-dichlorodiethyl selenide. It has been mentioned that when hydrobromic acid is added to a cold aqueous solution of ββ'-dichlorodiethyl selenide dichloride this dibromide is precipitated (see p. 1881) and the facts now brought forward prove that when ββ'-dichlorodiethyl selenide dichloride is dissolved in water the halogen atoms attached to the selenium are hydrolysed.

When a chloroform solution of selenium monochloride is added to a similar solution of ββ'-dichlorodiethyl selenide, selenium is at once precipitated and the filtered solution yields a quantitative amount of ββ'-dichlorodiethyl selenide dichloride. The reaction takes place with evolution of heat and proceeds according to the equation $Se_2Cl_2+(C_2H_4Cl)_2Se=(C_2H_4Cl)_2SeCl_2+2Se$.

When ββ'-dichlorodiethyl selenide is oxidised with nitric acid, the only product which has up to the present been isolated is ββ'-dichlorodiethyl selenide dichloride (identified by its melting point and crystalline form), part of the selenide being destroyed. An attempt to prepare the oxide by the action of ethylene on selenium oxychloride resulted in the formation of selenium dioxide and ββ'-dichlorodiethyl selenide dichloride, the selenium oxychloride reacting as an equimolecular mixture of selenium dioxide and selenium tetrachloride.

ββ'-*Dibromodiethyl Selenide*, $(CH_2Br{\cdot}CH_2)_2Se$.—This compound is prepared by reduction of ββ'-dibromodiethyl selenide dibromide by means of potassium metabisulphite under the conditions already described. It crystallises from ethyl alcohol in yellow needles, m. p. 44·2°, and is much more easily handled than the corresponding chloro-compound (Found: Br, 53·5. $C_4H_8Br_2Se$ requires Br, 54·2%).

It combines with chlorine in chloroform solution to give ββ'-*dibromodiethyl selenide dichloride*, $(C_2H_4Br)_2SeCl_2$, pale yellow prisms, m. p. 98—99°, from chloroform (Found: Cl+Br, 62·8. $C_4H_8Cl_2Br_2Se$ requires Cl+Br, 63·0%). This compound has a greater solubility in organic solvents than the analogous compounds already mentioned. The same compound is precipitated by adding a concentrated solution of hydrochloric acid to a cold aqueous solution of ββ'-dibromodiethyl selenide dibromide, but it has to be separated from some unchanged dibromide which is precipitated with it. As was expected, the melting point of the product so obtained was somewhat low (96°), but, on reduction, it gave ββ′-dibromodiethyl selenide identical with an authentic specimen.

Addendum.

The reaction between propylene and selenium tetrachloride has also been carried out. ββ′-Dichlorodipropyl selenide dichloride, m. p. 76·5° (Boord and Cope, *loc. cit.*, give 81°), was obtained in almost theoretical yield. It is conveniently purified by dissolving in cold water, in which it is readily soluble, and reprecipitating with hydrochloric acid (Found : Cl, 46·7 ; calc., Cl, 46·5%). When reduced with potassium metabisulphite under the usual conditions, it was converted into ββ′-dichlorodipropyl selenide, which has not yet been obtained crystalline (Found : Cl, 30·1 ; calc., Cl, 30·3%).

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[*Received, July* 13*th*, 1925.]