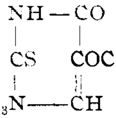
Two grams of chloracetic acid and 1 gram of 1-methyl-2-thio-5-hydroxyuracil were dissolved in boiling water and the solution evaporated to dryness. We obtained a crystalline compound, which separated from hot water in stout prisms, and decomposed at 217° with effervescence. It gave a strong test for sulphur and crystallized from water without water of crystallization. Analysis (Kjeldahl): Calculated for $C_7H_8O_4N_2S$, N 12.96; found, 12.8.

This pyrimidine was extremely stable in presence of hydrochloric acid. Some of the compound was dissolved in a large excess of concentrated acid and the solution evaporated to dryness. The pyrimidine was recovered unaltered and decomposed sharply at 217°. Analysis (Kjeldahl): Calculated for $C_7H_8O_4N_2S$, N 12.96; found, 12.94.

2-Thio-3-methyl-5-ethoxy-6-oxypyrimidine,



—This pyrimidine was obtained, in small amount, when the double compound of potassium iodide and 2-ethylmercapto-3-methyl-5-ethoxy-6-oxypyrimidine was digested with hydrochloric acid. After expelling the hydrochloric acid, we obtained a crystalline substance which was washed with alcohol and then crystallized from hot water. It separated in long needles which melted at 210–1° to an oil, without effervescence. It contained sulphur and gave a violet colored solution by treatment with bromine water and barium hydroxide. Analysis (Kjeldahl): Calculated for $C_7H_{10}O_2N_2S$, N 15.05; found, 15.05.

NEW HAVEN, CONN.

THE SLOW OXIDATION OF 2,2-DICHLORVINYL ETHYL ETHER.[1]

BY WILLIAM FOSTER.

Received March 19, 1909.

I. Introduction.—It is well known that halogen substitution products of ethylene, such as dibromethylene, $CH_2:CBr_2$, undergo oxidation even on exposure to the air—$2CH_2:CBr_2 + O_2 \longrightarrow 2CH_2Br.COBr$.[2]

By the oxidation of compounds of this type, there appears to be a direct absorption of oxygen with the formation of an acid chloride, bromide or fluoride.

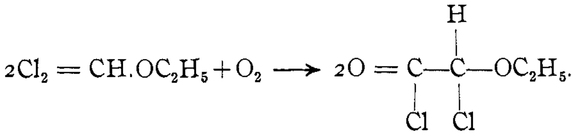
Halogenated vinyl ethyl ethers, at least some of them, are also susceptible of oxidation by treatment with oxygen, but they have not been thoroughly investigated.

At the suggestion of Professor Fred Neher, the author has made a careful study of the action of oxygen gas on 2,2-dichlorvinyl ethyl ether, $CCl_2:CH.OC_2H_5$, and the main facts observed in connection with the oxidation may be expressed by the following equations:

---

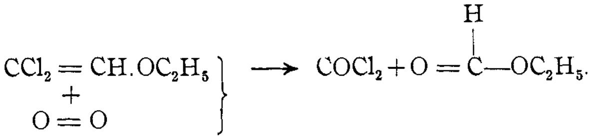
[1] Read before the New York Section of the American Chemical Society, March 5, 1909.

[2] Demole, *Ber.*, 11, 316, 1307.

1.


$$2Cl_2 = CH.OC_2H_5 + O_2 \longrightarrow 2O = \underset{Cl}{C}-\underset{Cl}{\overset{H}{C}}-OC_2H_5.$$

Ethoxychloracetyl chloride.

2.


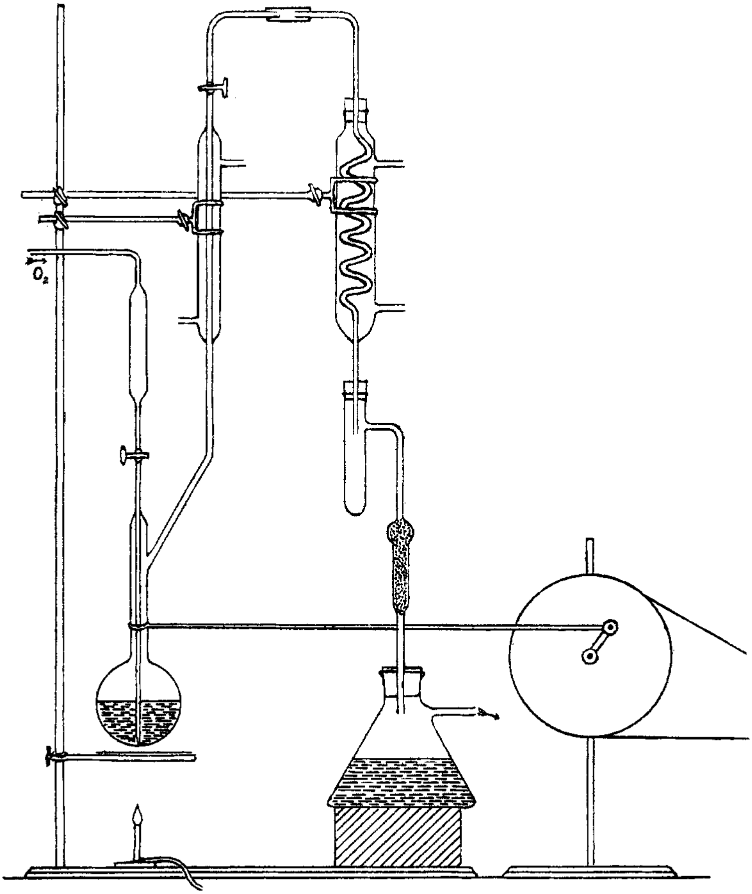
$$\left.\begin{array}{c} CCl_2 = CH.OC_2H_5 \\ + \\ O=O \end{array}\right\} \longrightarrow COCl_2 + O = \overset{H}{C}-OC_2H_5.$$

Phosgene. Ethyl formate.

According to the first equation there is a direct absorption of oxygen with the formation of ethoxychloracetyl chloride. I do not find this acid chloride described in the literature. From the action of oxygen on the halogen substitution products of ethylene, this result would have been anticipated. According to the second equation, it is seen that the double bond of dichlorvinyl ethyl ether is broken and one atom of oxygen from the molecule adds on to the end of the chain to form phosgene and on to the other end to form ethyl formate.

II. Apparatus and General Method of Carrying out the Oxidation.—On passing dry oxygen gas into the dichlorvinyl ethyl ether contained in a flask, it was soon observed that the gas was absorbed, the absorption being accompanied by a decided rise in the temperature, but in the course of time, the absorption of the gas decreased with a consequent fall in the temperature. It was also observed that corrosive fumes (carbonyl chloride) were formed, which appeared to collect in the flask and to interfere with the further oxidation of the compound. It was, therefore, necessary to devise a shaking apparatus connected with the oxygen reservoir, so constructed as to keep the liquid in a violent state of agitation and provided with an arrangement for absorbing or conducting away the fumes. The following apparatus, for which I am partially indebted to Professor G. A. Hulett, was constructed (see fig.).

A 300 cc. distillation flask was chosen, and a tube fitted with a cock was passed through the neck of the flask until its lower end was 2 or 3 mm. from the bottom of the flask. The tube and neck of the flask were then fused together. The arm of the flask was bent at an angle of about 30° and fused to a condenser tube, and the upper end of the condenser tube was fused to a second cock. The condenser near the upper end of the jacket was fastened in a clamp firmly borne by a heavy standard. The clamp had a screw-joint near the condenser, which permitted of a free wrist-like movement. A metal rod was fastened by one end to the neck of the flask, the other end being connected with an eccentric, which was operated by a small hot-air or electric motor. In carrying out the earlier experiments, the outlet of the condenser was connected with a train of bottles and tubes containing various absorbents, but in later experiments it was found more convenient to connect the shaker with a second condenser (see fig.) bearing a test-tube with a side arm at its upper end. The arm of the test-tube was connected with a calcium chloride tube which connected with a filter flask containing water, and the arm of this flask was connected with a lead pipe through which water ran to the sink. It was thus possible to take care of the escaping vapors and gases and also to condense liquids of low boiling points. Even with this shaker it required several days to completely oxidize 40–50 grams of the ether, and two or three weeks to completely oxidize 100–150 grams. This shaker was found to be very satisfactory indeed, and it was possible, when desirable, to keep the oxidation going on continuously day and night.



III. Experimental. (*a*) *Formation of Ethoxychloracetyl Chloride.*—From the large number of tedious experiments carried out a few will now be cited in order to present the main facts observed in connection with the oxidation of dichlorvinyl ethyl ether. Large quantities of the ether were needed and it was prepared according to the method of Neher and Foster.[1]

Experiment 1—Forty grams dichlorvinyl ethyl ether contained in the flask of the shaker were treated with dry oxygen gas. At the beginning of the experiment the gas was absorbed at a fair rate, the absorption being accompanied by a very decided rise in the temperature, but soon it was absorbed more slowly and in the course of time it almost ceased to flow in. After opening the outer cock and running in oxygen and sweeping out the vapors which had accumulated and then closing the cock again, the gas was once more rapidly absorbed. The vapor proved to be carbonyl chloride, $COCl_2$. This treatment of the liquid with oxygen was kept up for four days, when the absorption of the gas seemed to be at an end and the oxidation was assumed to be complete. A distillation under diminished pressure was carried out and 26 grams of a clear colorless liquid were obtained, the larger fraction collecting at 57–8° and at a pressure of 16–7 mm. There was a small residue and but little decomposition. The main fraction (13.5 grams) was redistilled, and the first and largest fraction (8.2 grams) condensed at 53–5° and at 15 mm. Analysis:

Calculated for $(C_2H_3OCl)_n$:	C, 30.57; H, 3.86; Cl, 45.16
Found:	C, 30.45; H, 3.83; Cl, 45.69

The liquid was clear and colorless and heavier than water. It had a disagreeable, penetrating odor and was readily hydrolyzed, all of which went to show that it was an acid chloride. It appears therefore that dichlorvinyl ethyl ether absorbs oxygen directly with the formation of ethoxychloracetyl chloride, as shown in the *Introduction*, Equation 1.

Experiment 2.—Seventy-four grams of the ether were treated with oxygen very much as in Expt. 1, but at the end of three days the flask was warmed up to 50–60° by means of a small burner, and the oxidation was kept up with occasional heating for four days more. On fractionation, about 55 grams were obtained, the largest fraction condensing at 55–60° and at 16–7 mm. On redistilling the chief fraction (39.8 grams), 37.8 grams were obtained, the main fraction condensing at 58–9° and at 18–20 mm. Analysis:

Calculated for $(C_2H_3OCl)_n$:	C, 30.57; H, 3.86; Cl, 45.16
Found:	C, 30.26; H, 3.95; Cl, 46.15

This agrees fairly well with the first analysis, but the chlorine is about 1 per cent. high, which may be largely due to the presence of a small amount of phosgene which is formed by the oxidation of the ether and which appears to be somewhat soluble in the acid chloride. The fraction of the liquid with the above analysis distilled at atmospheric pressure at 148–58°, mostly at 151–3°, and there was but little apparent decomposition. By hydrolyzing a small sample of the liquid it was ascertained that there was a small residue insoluble in water, which proved to be dichlorvinyl ethyl ether, thus showing that the oxidation was not quite complete.

Experiment 3.—To insure the complete oxidation of the ether it was determined to pass oxygen into the liquid with gentle heating and shaking until a few drops of it would be thoroughly decomposed by and completely soluble in water. Provision was also made for absorbing the carbonyl chloride and the excess of oxygen, and to find out if any other vapor or gas could be collected over water. Accordingly, 95 g. of the ether were run into the flask and oxygen permitted to bubble through the liquid as in Expt. 2. To get rid of the carbonyl chloride and also to adsorb the excess of

---

[1] THIS JOURNAL, **31**, 412 (1909).

oxygen escaping with it, the vapors were passed through a train of bottles and tubes containing water, wet cotton, and alkaline solutions of pyrogallol. At the end of this train, it was found that a gas or vapor collected *slowly* over water. It possessed an ethereal odor and burned with a green flame. It failed to support combustion, contained no phosgene, and answered to the usual tests for ethyl chloride. By keeping the flask at a temperature of 60–70° and continuing to pass in oxygen for about two weeks, the oxidation was found to be complete; at all events the liquid was completely decomposed by and soluble in water. On fractionation, 47 g. were obtained, mostly at 55–8° and at 12–15 mm. On redistilling, the larger fraction condensed at 53–4° and at 11 mm. It was believed that this fraction was quite free from any of the chlorinated ethers. Analysis:

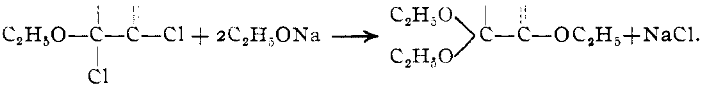
Calculated for $(C_2H_3OCl)_n$:	C, 30.57; H, 3.86; Cl, 45.16
Found:	C, 30.15; H, 3.96; Cl, 45.84

The molecular weight of samples of the above fraction was determined for me by T. S. Woodward. The average result by the Bleier and Cohn modification of the Victor Meyer method was 158.7; by the freezing point method in benzene, it was 161.6. This showed that the molecular formula for the acid chloride was $C_4H_6Cl_2O_2$. The molecular weight of this compound would be 157.

The substance was thoroughly tested with various reagents and found to possess all the properties of acid chlorides. Dichlorvinyl ethyl ether, therefore, absorbs oxygen directly, forming ethoxychloracetyl chloride, the structure of which will be proved below to be $C_2H_5O.CClH.COCl$. The acid chloride is a clear, colorless, fuming liquid. Its specific gravity at 18°/4° is 1.2639. At a pressure of 11 mm. the purest sample obtained boiled at 53–4°. At atmospheric pressure, it boils in the vicinity of 150°.

(*b*) *Structure of Ethoxychloracetyl chloride.*—As stated above, the chloride possesses the characteristic properties of the acid chlorides. It reacts readily with water and vigorously with ammonia, aniline, and alcohol. Several attempts were made to prepare salts of ethoxychloracetic acid, but thus far no very consistent results have been obtained. The acid chloride was treated with ethyl alcohol in varying quantities and under different conditions, and while an ester was obtained in every case, the analyses did not agree well, and it was concluded that a mixture was obtained, and that the acid chloride had a tendency to exchange both of its chlorine atoms for the ethoxy group. It was, therefore, determined wholly to replace, if possible, both the chlorine atoms with the ethoxy group by the use of an alcoholic solution of sodium ethylate. A number of experiments were made, one of which will now be cited:

4.4 g. sodium were dissolved in 75 cc. of absolute alcohol, and 15.2 g. of the acid chloride (theory = 15 g.) were run in drop by drop at a temperature below 10°. Much sodium chloride separated out. The mixture stood over night in an ice-box. In the morning it was still alkaline, so it was heated on the water-bath for one and one fourth hours, when it was still mildly alkaline. The mixture was worked up with ethyl ether and cold water, the ether solution of the ester was separated and dried over anhydrous sodium sulphate, and then fractionated. 7 g. of liquid were obtained at 85–92° and at 14–15 mm. It was clear and colorless, possessed a fragrant odor and a burning taste, and was almost free from chlorine. At atmospheric pressure it boiled at 190–5°. Assuming the structure of the acid chloride already given and that both of its chlorine atoms are replaced by the ethoxy group, we have the following equation:



$$C_2H_5O-\underset{\displaystyle Cl}{\overset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-Cl + 2C_2H_5ONa \longrightarrow \begin{matrix}C_2H_5O\\ C_2H_5O\end{matrix}\!\!>\overset{\displaystyle H}{C}-\overset{\displaystyle O}{\overset{\|}{C}}-OC_2H_5+NaCl.$$

Ethoxychloracetyl chloride. Ethyl ester of diethoxyacetic acid.

The ethyl ester of diethoxyacetic acid is known. It is described in Beilstein, 3rd Ed., Vol. I, p. 631. The compound was prepared by Schreiber,[1] and also by Pinner and Klein,[2] by totally different methods. Schreiber gives its boiling point as 199.2° and its specific gravity as 0.994 at 18°. Pinner and Klein found the boiling point to be 195°. Analysis:

Calculated for $C_8H_{16}O_4$:	C, 54.51; H, 9.16
Found:	C, 53.42; H, 8.97

The carbon according to this analysis is about one per cent. low. The specific gravity of the liquid was 1.0030 (18°/4°). Without further attempts to purify the compound and to make other analyses of it, it was determined to prepare, if possible, some known derivative of the ester. The corresponding amide was prepared by Schreiber[3] and by Pinner and Klein.[3] Schreiber obtained it by treating the ethyl ester of diethoxyacetic acid with ammonia and alcohol:

$$(C_2H_5O)_2CHCOOC_2H_5 + NH_3 \longrightarrow (C_2H_5O)_2CH.CO.NH_2 + C_2H_5OH.$$

The following experiment was next carried out: 1.5 g. of the ester were treated with 2 cc. absolute alcohol and 2 cc. strong ammonia water. The mixture stood at room temperature for 24 hours, and was then evaporated over sulphuric acid under diminished pressure until crystallization was brought about. The crystals, which were white, transparent, flexible, greasy plates, melted at 78–9°. They had a bitter, salty taste and were rapidly soluble in water, alcohol, and ether. On crystallization from alcohol, the melting point was 80–1°. Schreiber gives it as 76.5°, and Pinner and Klein as 81–2°. All the properties of this amide corresponded well with those of the compound described in the literature. It was evident, therefore, that the acid chloride contains two atoms of replaceable chlorine and that it is closely related to acetyl chloride, and accordingly has the structure given below.

IV. The Mechanism of the Oxidation.—In conducting the various experiments on the oxidation of the ether, there were indications that a liquid with a low boiling point was formed along with phosgene. To determine whether this was true and to explain, if possible, the formation of phosgene, the following experiment was carried out: 75 g. of ether were treated with oxygen for four days as in the previous experiments, but without the application of heat. The flask was then heated up to about 75° for a short while, and the escaping vapors were partially condensed in the worm condenser. About 4 cc. of distillate collected in the test-tube attached to the condenser. On fractionation, it distilled at 21–57.5°, about two-thirds condensing at 52–7.5°. All the fractions gave the usual tests for phosgene (boiling point 8°), which was present in considerable amounts in the first fraction. A few drops of the fraction with the higher boiling point were treated with a solution of potassium hydroxide until the disagreeable odor of phosgene had entirely disappeared, whereupon the strong agreeable odor of an ester was very evident. The substance answered to the tests for formic acid, so it was clear that it was ethyl formate (boiling point 53–4°).

By the slow oxidation of 2,2-dichlorvinyl ethyl ether, the chief products formed are three, namely, ethoxychloracetyl chloride (a new compound), phosgene, and ethyl formate. Ethyl chloride also seems to be formed in small amount. It is not as yet possible to state positively just what is the mechanism of the oxidation. We may look at it as represented in equations 1 and 2 in the *Introduction*, or we may consider that it takes

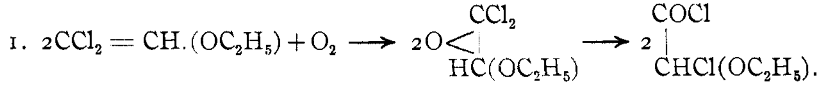
---

[1] *Zeitschrift f. Chemie*, 1870, 167.

[2] *Ber.*, 11, 1475.

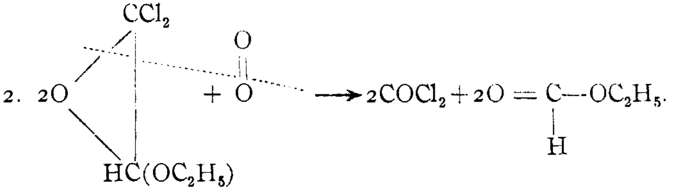
[3] *Loc. cit.*

place with the formation of unstable ethylene oxide derivatives as suggested by Henry[1] and advocated by Swarts[2] for the oxidation of the halogen derivatives of ethylene. Or again, as suggested to the author by Professor Neher, we may regard the oxidation as taking place by the addition of half broken oxygen molecules (—O—O—) to form an unstable compound of the peroxide type somewhat after the manner assumed by Engler and Wild[3] in the case of the compounds whose autoxidation they investigated. The splitting off of an oxygen atom from the unstable peroxide may then be accompanied by the transposition of a chlorine atom to form ethoxychloracetyl chloride. On the other hand, some of the peroxide molecules may break down directly into phosgene and ethyl formate. According to the former plan, the oxidation may be represented by the following equations:



$$1.\ 2CCl_2 = CH.(OC_2H_5) + O_2 \longrightarrow 2O<\begin{matrix}CCl_2\\ |\\ HC(OC_2H_5)\end{matrix} \longrightarrow 2\begin{matrix}COCl\\ |\\ CHCl(OC_2H_5).\end{matrix}$$

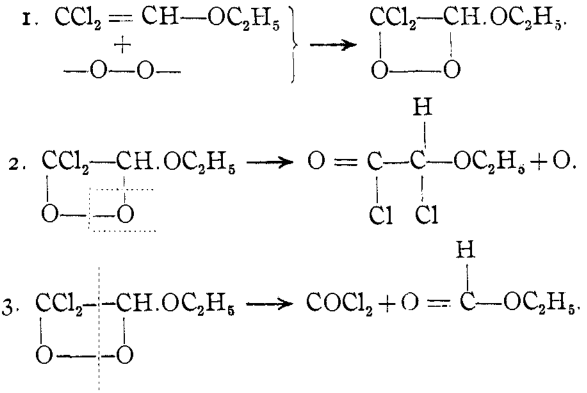
Ethoxychloracetyl chloride.



$$2.\ 2O\begin{matrix}CCl_2\\ |\\ HC(OC_2H_5)\end{matrix} + \begin{matrix}O\\ \|\\ O\end{matrix} \longrightarrow 2COCl_2 + 2O = \begin{matrix}C—OC_2H_5.\\ |\\ H\end{matrix}$$

Ethyl formate.

According to the second hypothesis, the changes may be represented somewhat more simply as follows:



$$1.\ \left.\begin{matrix}CCl_2 = CH—OC_2H_5\\ +\\ —O—O—\end{matrix}\right\} \longrightarrow \begin{matrix}CCl_2—CH.OC_2H_5.\\ |\qquad\quad |\\ O——O\end{matrix}$$

$$2.\ \begin{matrix}CCl_2—CH.OC_2H_5\\ |\qquad\quad |\\ O—\,—O\end{matrix} \longrightarrow O = \begin{matrix} & H\\ & |\\ C— & C—OC_2H_5 + O.\\ | & |\\ Cl & Cl\end{matrix}$$

$$3.\ \begin{matrix}CCl_2—\,—CH.OC_2H_5\\ |\qquad |\\ O——\,—O\end{matrix} \longrightarrow COCl_2 + O = \begin{matrix}H\\ |\\ C—OC_2H_5.\end{matrix}$$

In conclusion, I wish to express my thanks to Professor Neher for his interest in the work and for his valuable suggestions from time to time.

PRINCETON UNIVERSITY, March 5, 1909.

---

[1] *Ber.*, 12, 1838–1844 (1879).

[2] *Bull. Acad. roy. Belgique* [3], 36, 532–52 (1898).

[3] *Ber.*, 30, 1669 (1897).