Numerous other preparations gave yields running in every case except one from 55 per cent. to 74 per cent. of the theoretical. The method has since been most successfully employed by the Baker and Adamson Chemical Co. to prepare kilogram quantities of the compound for the authors.

The compound distils without decomposition even at atmospheric pressure and keeps well in a sealed glass tube.

II. The Boiling Point and Specific Gravity of Tetrachlorether.—1. A sample of tetrachlorether prepared as above described and collected from 180°–189°, mostly at 188°, was found to have a specific gravity of 1.4195. This determination, like all others given in this article, was carried out in a Sprengel-Ostwald pycnometer at 18° and reduced to water at 4° and to vacuum. On redistillation of this sample a fraction collected at 188°–189° showed a specific gravity of 1.4224.

Analysis: calculated for $C_4H_6OCl_4$ C, 22.65; H, 2.86
Found: C, 22.48; H, 2.80

The above preparation of tetrachlorether was kept in a sealed tube for about eight and a half months and then redistilled. It boiled almost constantly at 188° under a barometric pressure of 756.4 mm. Its specific gravity was found to be 1.4226.

2. A sample of tetrachlorether from another preparation was collected at 188° and showed a specific gravity of 1.4224. The liquid was redistilled and a fraction boiling constantly at 188° at 755.2 mm. barometric pressure gave a specific gravity of 1.4227. The boiling point of this sample, which was regarded as especially pure, was determined in an apparatus permitting the mercury of the thermometer to be completely immersed in the vapor of the boiling liquid and found to be 189.4° at 749.1 mm. (corrected). This is in close agreement with the value given in Beilstein, 3Ed., Vol. I., p. 296—namely, 189.7° at 758.7 mm.

The average of the four determinations of the specific gravity of pure tetrachlorether at 18°/4° given above is 1.4225, which is to be taken as the most probable value. Henry[1] found it to be 1.4211 at 15°; in Beilstein (p. 296) it is given as 1.4379 at 0° and as 1.4182 at 15.2°.

3. A sample of tetrachlorether that boiled constantly at 189° under atmospheric pressure was found to boil at 79° under a pressure of 16 mm.

Analysis: calculated for $C_4H_6OCl_4$ C, 22.65; H, 2.86
Found: C, 22.51; H, 2.77

PRINCETON UNIVERSITY, Dec 30, 1908.

2,2-DICHLORVINYLETHYLETHER: ITS PREPARATION FROM TETRACHLORETHER AND ITS PHYSICAL PROPERTIES.

BY FRED NEHER AND WILLIAM FOSTER.

Received January 14, 1909

2,2-Dichlorvinylethylether, $CCl_2:CH.OC_2H_5$, was first prepared by

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[1] *Ber.*, 4, 102.

Godefroy,[1] who obtained the compound by heating 1,2,2-trichlorether with an excess of a 1:1 aqueous solution of potassium hydroxide. The yield was good, about 75 per cent. of the theoretical, and the product quite pure. Godefroy simply states that the compound is a liquid boiling at about 145° under normal pressure, heavier than water and insoluble in it; that it reduces silver nitrate, but does not react with ammonia, sodium hydrogen sulphite or potassium hydroxide; and that it readily absorbs the halogens, forming with chlorine the tetrachlorether obtained by Henry[2] by the action of phosphorus pentachloride on chloral alcoholate, from which he deduces the structure of the compound. Swarts[3] obtained the same compound by heating dichlorfluorethylene with sodium ethylate at 130°. Oddo and Mameli,[4] having improved the method for preparing trichlorether, tried Godefroy's reaction, but failed to obtain any dichlorvinylether by it, possibly because they did not use a sufficiently concentrated solution of potassium hydroxide. They did obtain Godefroy's compound, however, by long continued boiling (215 hours) of trichlorether alone, as also, in poor yield, by heating it with sodium methylate, or with a methyl alcohol solution of potassium hydroxide. They give the boiling point as 144°-146° and the specific gravity as 1.221 (15°).

In the course of some experiments on Henry's tetrachlorether undertaken by one of the authors[5] at the suggestion of Professor Nef of the University of Chicago, it was found that an alcoholic solution of this compound is readily acted upon by zinc to form either 2,2-dichlorvinylethylether or dichloracetal according to the conditions of reaction. The formation of dichloracetal by this method, which has been shown to involve the direct addition of alcohol on dichlorvinylether, will be discussed in an article soon to be published in THIS JOURNAL. The present article deals only with the preparation and properties of dichlorvinylether

I. The Preparation of Dichlorvinylether by the Action of Zinc on Tetrachlorether.—When granulated zinc is added to tetrachlorether dissolved in alcohol, reaction at once sets in and the temperature of the solution rises more or less rapidly and markedly according to the proportion of alcohol present. Zinc chloride is formed, but remains in solution. No gas is given off. This is in marked contrast to the behavior of 1,2-dichlorether, which, under similar conditions, evolves hydrogen and yields chloracetal. If the alcoholic solution be not too concentrated, *i. e.*, containing not less than 5 molecules of alcohol to one molecule of tetrachlorether, and the temperature of the mixture be kept below 40°, practically

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[1] *Compt. rend.*, **102**, 869; *Jsb. Chem.*, **1886**, 1174; Thèse, Paris, 1886, p. 89.

[2] *Ber.*, **4**, 101.

[3] *Chem. Centr.*, **1903**, I, 13.

[4] *Gazz. chim. ital.*, **33**, II, 373; *Chem. Centr.*, **1904**, I, 921.

[5] Neher.

the only products of the reaction are zinc chloride and dichlorvinylether:

$$CCl_3CClH.OC_2H_5 + Zn = CCl_2:CH.OC_2H_5 + ZnCl_2.$$

But when the temperature of the reacting mixture is allowed to rise without much restraint, or the mixture, after the completion of the reaction, is digested for a long time on the water bath, especially if the solution be concentrated, an addition of alcohol on the dichlorvinylether takes place, which is favored by the presence of the zinc chloride, and the resulting product consists more or less completely of dichloracetal,

$$CCl_3CClH.OC_2H_5 + Zn + C_2H_5OH = CCl_2H.CH(OC_2H_5)_2 + ZnCl_2.$$

This is shown very clearly in the results of two of the early experiments with this reaction, *viz.*:

1. An excess of granulated zinc was added to a solution of 54 g. of tetrachlorether[1] in 75 g. of alcohol (about 6½ molecules) and the mixture kept moderately cool by shaking under the tap. After the reaction slackened, the mixture was allowed to stand over night and then was heated for one hour on the water bath under a reflux condenser. The product was worked up by diluting with water, separating the oil and washing, drying and distilling it in the usual manner. Practically all the liquid boiled between 143° and 147°, most of it between 144° and 145°. The yield was 21.5 g. or 60 per cent. of the theoretical. The product exhibited all the properties of Godefroy's compound.

2. 71.5 g. of tetrachlorether dissolved in 50 g. of alcohol (about $3^1/_4$ molecules) were treated with zinc with but slight cooling, the mixture allowed to stand over night and then heated for one hour on the water bath. The coffee-colored liquid was treated with water and the precipitated oil separated, washed, dried and distilled. Instead of dichlorvinylether, 39 g. of a product boiling from 183°–195° and consisting principally of dichloracetal were obtained. It is, therefore, not advisable to digest the reaction mixture on the water bath.

Subsequently it was also found that the dichlorvinylether prepared and collected as above described was not, or at least did not long remain, strictly pure, owing to the great readiness with which it absorbs oxygen even from the air. This spontaneous oxidation of dichlorvinylether, together with its products, has been studied in detail by one of the authors,[2] who will shortly present his results in THIS JOURNAL. Suffice it to state here that this susceptibility to oxidation necessitates special care at all stages in protecting the product from air.

After much experimenting a method of operating has been developed which insures a yield of 80–90 per cent. of the theoretical. This may best

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[1] For an improved method for the preparation of tetrachlorether see the preceding article.

[2] Foster.

be described perhaps by citing a typical trial of it. 135 g. of granulated zinc were placed in a roomy flask fitted with a three-hole stopper bearing a thermometer, a tube through which carbon dioxide was introduced, and a vent. A solution of 135 g. of tetrachlorether in 188 g. of absolute alcohol (about 6.4 molecules) was then added and the flask gently shaken, with just enough cooling under the tap to maintain the temperature at 30–40° during the progress of the reaction. After the reaction had subsided, the flask was tightly stoppered and allowed to stand over night at room temperature. In the morning 110 g. of zinc oxide[1] suspended in 1350 cc. of water were added. The mixture was then subjected to a steam distillation in an atmosphere of carbon dioxide. The dichlorvinylether passed over rapidly and, when all over, was separated from the mixture of water and alcohol floating above it in the receiver and washed, 78.5 g. of the crude product being thus obtained. It was discovered, however, that the aqueous alcoholic portion of the distillate still contained dichlorvinylether in solution and 8 g. of the latter were recovered from it by the addition of water. The whole yield of crude oil was thus 86.5 g. This was dried over calcium chloride and fractionated. 81.1 g. of distillate were collected between 140° and 150°, making a yield of 90 per cent. of the theoretical.

II. The Specific Gravity and Boiling Point of Dichlorvinylethylether.—Some of the dichlorvinylether from the above described preparation was carefully redistilled and a sample obtained which boiled quite constantly at 145°. The boiling point of what was regarded as the purest fraction was then determined in an apparatus which permitted the mercury of the thermometer to be completely immersed in the vapor of the boiling liquid, and found to be 144.2° at 765.3 mm. (corrected).

The specific gravity of a considerable quantity of the liquid redistilled at constant boiling point (145°) was determined in a Sprengel-Ostwald pycnometer and reduced to water at 4° and to vacuum. It was found to be 1.2101 at 18° and 1.2087 at 20°.

A portion of this dichlorvinylether was again redistilled and its specific gravity again determined and found to be 1.2090 at 18°/4° and 1.2075 at 20°/4°.

The averages of these determinations are 1.2096 (18°/4°) and 1.2081 (20°/4°). Oddo and Mameli[2] give the value 1.221 (15°).

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[1] In other experiments sodium carbonate solution and magnesium oxide suspended in water were used to neutralize the reaction mixture prior to the steam distillation, but with much less satisfactory results.

[2] *Chem. Centr.*, **1904**, I, 921.