SCIENTIFIC SECTION

PREPARATION OF DIVINYL ETHER.

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During the last decade, since the substance $\beta\beta'$-dichloroethyl ether has become readily accessible, the preparation of divinyl ether from it has been accomplished by three groups of workers.

Cretcher and Pittenger (1) were the first to accomplish this. They made the interesting discovery that the reaction between $\beta\beta'$-dichloroethyl ether and the sodium alcoholates of certain primary alcohols of low molecular weight, carried out by refluxing in an excess of the alcohol, did not result in the withdrawal of hydrogen chloride from the dichloroethyl ether to form divinyl ether, but proceeded by the mechanism of the Williamson synthesis to give the ethers of the general formula $ROCH_2CH_2OCH_2CH_2OR$, or, when an excess of the $\beta\beta'$-dichloroethyl ether was present, the half ethers $ROCH_2CH_2OCH_2CH_2Cl$. In this manner they produced in good yield the ethers

β-chloro-β'-methoxy diethyl ether
Bis (β-methoxy) diethyl ether
Bis (β-ethoxy) diethyl ether
Bis (β-propoxy) diethyl ether
Bis (β-butoxy) diethyl ether

They found, however, that when $\beta\beta'$-dichloroethyl ether was digested with heated sodium hydroxide without the presence of an hydroxylated solvent it suffered the loss of one or two molecules of hydrogen chloride to give some vinyl ethyl ether and some divinyl ether. They reported also the formation of acetaldehyde as a by-product.

Hibbert, Perry and Taylor (2) confirmed the findings of Cretcher, *et al.*, in that they too obtained vinyl ethyl ether, divinyl ether and acetaldehyde when $\beta\beta'$-dichloroethyl ether was digested with solid potassium hydroxide at elevated temperatures.

Ruigh and Major (3) improved the method of Hibbert (2), *et al.*, by adding the $\beta\beta'$-dichloroethyl ether gradually to the vigorously agitated molten potassium hydroxide. In this way they were able to obtain yields of 21% and better of divinyl ether. By the use of suitable apparatus they effected a fractionation of the products of the reaction so that a considerable portion of the chloroethyl vinyl ether refluxed back into the reactor while the divinyl ether as well as the low boiling impurities, *viz.*, acetaldehyde and ethylene oxide continued on to a condenser in which all but the gaseous impurities were finally condensed. They also found that a small stream of gaseous ammonia continuously passed through the system repressed the formation of acetaldehyde somewhat.

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In considering the experiences of these several authors it seemed at the outset that a method by which the withdrawal of two molecules of hydrogen chloride from the ββ'-dichloroethyl ether could be carried out by means of potassium hydroxide or a similar alkaline substance in a homogeneous reaction mixture through the use of a suitable solvent would be much more controllable and might obviate to a large degree the many possible side reactions. To devise such a method we needed to provide a solvent which could dissolve an alkali such as potassium hydroxide as well as the organic substance ββ'-dichloroethyl ether. Only an hydroxylated solvent such as an alcohol could be expected to do this and we therefore subjected a quantity of ββ'-dichloroethyl ether to the action of alcoholic potassium hydroxide. It was found, however, that here, too, a condensation reaction occurs between the dichloroethyl ether and the alcohol to give Bis (β-ethoxy) diethyl ether and no withdrawal of hydrogen chloride to give divinyl ether. Further consideration of the subject, however, suggested the use of such alcohols, or hydroxylated solvents in general, which would not react according to the Williamson synthesis due either to excessive molecular weight or some structural peculiarity. In general an alcohol of C_5 or greater would be expected to form ethers by condensation with alkyl halides (Williamson synthesis) only with great difficulty. Also one would expect secondary alcohols to form ethers by this mechanism with considerable difficulty; and tertiary alcohols almost not at all. In addition to non-participation in the Williamson reaction a suitable hydroxylated solvent is needed to fulfil the additional requirement of dissolving generous concentrations of potassium hydroxide as well as the dichloroethyl ether. It was expected that this difficulty would be hard to meet for it was not at all to be expected that an alcohol of C_5 or more would dissolve any significant quantities of potassium hydroxide. For this reason it was decided to make the first attempt with the dihydroxylated solvent, diethylene glycol (ββ'-dihydroxy ethyl ether); and, we were able to obtain a yield of 25% of divinyl ether by the gradual addition of dichloroethyl ether to a refluxing solution of potassium hydroxide in this solvent.

This experiment was of considerable interest in that we were able to obtain yields of divinyl ether comparable to those of Ruigh and Major (3) despite the fact that we were using potassium hydroxide dissolved in an alcohol, the alcohol having been so chosen that the difficulty due to etherification reported by them was obviated. The method was not altogether satisfactory, however, since the yield of divinyl ether was not markedly increased over theirs and since the formation of acetaldehyde and gaseous decomposition products was not eliminated.

Our attention was then attracted to a rather interesting primary octyl alcohol, *viz.*, 2-ethyl hexyl alcohol, which had recently become an article of commerce. Its high molecular weight seemed to exclude any probability of its undergoing ether formation and we therefore determined the solubility of potassium hydroxide in this solvent. We were considerably surprised to find that this solubility was about 6% at 110° and became considerably higher as the temperature was elevated above that point. In an experiment in which dichloroethyl ether was added to a solution of potassium hydroxide in 2-ethyl hexyl alcohol we obtained a yield of 31–32% divinyl ether with almost no acetaldehyde or other volatile impurities in the distillate. Control of the reaction was at no time difficult and purification of the crude yield a very simple matter. The apparatus can be set up out of ordinary laboratory glassware in very short time and the experiment carried out in a few hours.

In view of the fact that interference with these reactions due to ether formation did not occur, it was now decided to attempt the elimination of hydrogen chloride from the dichloroethyl ether to form divinyl ether by means of sodium alcoholates dissolved in an excess of the corresponding alcohols. In doing so we again avoided the primary alcohols of low molecular weight such as were used by Cretcher, *et al.* (1), and again selected such alcohols as would be expected to resist etherification by the Williamson reaction. Tertiary butyl, tertiary amyl and tertiary hexyl alcohols were chosen because of their tertiary stucture, and the primary alcohol 2-ethyl hexanol due to its high molecular weight. In the case of tertiary butyl alcohol only a very poor yield of divinyl ether was obtained. Possible reasons for this poor result were the low attainable reaction temperature or the low solubility of sodium tertiary butyl alcoholate in that alcohol. The addition of dichloroethyl ether to solutions of the corresponding sodium alcoholates in all of the other alcohols, however, gave very satisfactory yields of divinyl ether. Due to the absence of side reactions the crude product contained only traces of acetaldehyde or other volatile impurities so that its purification was a very simple matter. Practically no gaseous decomposition products were formed, so that the reaction and delivery of product were at all times smooth and controllable.

It should be added that in no case did we try to extend our experiments beyond preliminary stages so that the results reported including yields are all amenable to considerable improvement by further study.

EXPERIMENTAL.

1. First Method—Reaction between $\beta\beta'$-dichloroethyl ether and potassium hydroxide dissolved in diethylene glycol.

This method was carried out on a considerably larger scale than any of the other methods to be described. Though somewhat different in design, the apparatus used was essentially the same as that described by Ruigh and Major (3). It consisted of an autoclave of about two gallon capacity equipped with an efficient agitator and charged at the outset of a run with the diethylene glycol solution of potassium hydroxide. Leading into this autoclave was a tube of small diameter through which the dichloroethyl ether could be injected. The feed rate of dichloroethyl ether was controlled by a valve and also by the pressure above the supply of this liquid in the reservoir, the variable pressure being conveniently obtained from a nitrogen cylinder. Leading into it also was another such tube through which a very small stream of ammonia was bled throughout the run. Leading from this autoclave was a reflux column of large capacity, about two inches in diameter and five feet long, in which most of the unreacted dichloroethyl ether and partially reacted β-chloroethyl vinyl ether was condensed and returned to the reaction mixture. Fairly substantial volumes of these incompletely reacted liquids escaped condensation in this reflux and for this circumstance there was provided a downward condenser from the top of the reflux column leading into a trap in which the additional condensate was retained. This condenser and trap were jacketed and held at 50° C. throughout the run. The uncondensed vapors were now led through a drying column and a downward coil condenser maintained below 0° C. into a receiver also at about 0° C. in which the divinyl ether and the volatile impurities such as acetaldehyde were accumulated. The uncondensable gases were led out doors through a flow meter so that any change in the amount of such gases was at once indicated.

In a typical run the autoclave was charged with one gallon of diethylene glycol and four pounds of 85% potassium hydroxide. During the course of three hours the theoretical quantity, 2415 Gm., of dichloroethyl ether was introduced into the reaction mixture, the temperature of the reaction being maintained at 200–210°, after a gradual increase from 180° C. during the first forty-five minutes.

After the reaction was complete a further addition of dichloroethyl ether resulted in the production of large quantities of acetaldehyde and gaseous decomposition products, the reaction mixture having become acidic.

The crude product obtained from the final condenser prior to the generation of the large quantities of acetaldehyde above referred to consisted of 150 cc. This product lost only 6 cc. during several treatments with dilute ammonia for the removal of acetaldehyde. Considering the necessary mechanical and evaporation losses, the amount of acetaldehyde contaminating the crude yield must have been very small. From a total of 790 cc. of non-aqueous liquid reclaimed from the trap, a fraction boiling below 70° C. (mostly below 40° C.) was obtained by distillation. This fraction consisted of 110 cc. and shrunk to 105 cc. after several treatments with dilute ammonia. A total crude yield of 249 cc. (200 Gm.) or about 21% of almost pure divinyl ether was therefore obtained.[1] After drying over calcium chloride and finally over sodium, this crude product was subjected to fractional distillation through an efficient rectifying column provided with a cooling jacket to avoid superheating of the divinyl ether vapor. In this manner a purified yield of 176 Gm. or 18.2% of pure divinyl ether boiling at 28° C. was obtained, most of the shrinkage having been due to handling losses. Practically no forerunnings or residue were recovered from the distillation.

2. Second Method—Reaction between $\beta\beta'$-dichloroethyl ether and potassium hydroxide dissolved in 2-ethylhexyl alcohol.

The apparatus in which this, and the subsequent experiments were carried out consisted merely of a 500-cc., three-neck flask equipped with an efficient mercury-sealed agitator, a dropping funnel for the dropwise addition of the dichloroethyl ether, and a reflux condenser. Following the reflux condenser was a downward spiral condenser and receiver, both of which units were cooled with ice water. At the exit end of the apparatus was a gasometer in which any gaseous decomposition products could be collected by the displacement of water.

A vigorously agitated solution of 75 Gm. of 85% potassium hydroxide dissolved in 450 cc. of 2-ethyl hexyl alcohol was heated to 135° C. and the dropwise addition of 81 Gm. of dichloroethyl ether commenced. The separation of potassium chloride was immediately observed. The temperature was then raised gradually while the addition of dichloroethyl ether was continued. At about 150° C. the condensation of product was observed in the receiver. After three hours, during which the reaction temperature was maintained at 150–155° C., the addition of the dichloroethyl ether was complete. The non-aqueous portion of the condensate consisting of 35 cc. was treated with several portions of dilute ammonia, washed with water and dried with calcium chloride followed by sodium. There was no pronounced odor of acetaldehyde in the crude product and practically no shrinkage occurred during the treatment with dilute ammonia.

Fractional distillation in ordinary equipment gave the following fractions:

Fraction 1	16 cc. between 29– 40° C.
Fraction 2	4 cc. between 100–125° C.
Fraction 3	6 cc. between 160–180° C.
Residue	7 cc.
Total	33 cc.

The higher boiling fractions consisted, no doubt, of dichloroethyl ether, 2-ethyl hexyl alcohol and perhaps a small quantity of β-dichloroethyl vinyl ether. Fraction 1 upon redistillation in the equipment previously described in which divinyl ether can be distilled without superheating gave 11 cc. of divinyl ether boiling at

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[1] It has been shown elsewhere, *C. A.*, 28, 5401 (1934), that pure divinyl ether will boil well above its boiling point of 28° C. unless special precautions are taken to avoid superheating, and that inconsequentially small traces of impurities arising from the reaction can elevate this boiling even up to 70° C.

27.8–28.6° C. and no liquid was discernible in the flask at the end of the distillation. Upon cooling the distillation flask 2.3 cc. of liquid condensed back into it. It is our belief that this residue was also substantially pure divinyl ether and that the only shrinkage from the yield previous to this last distillation was due to the obviously necessary mechanical losses. Calculated on a basis of the 16 cc. in hand before this step we therefore had a yield of 31–32% of theory.

3. Third Method—Reaction between $\beta\beta'$-dichloroethyl ether and sodium tertiary butylate dissolved in tertiary butyl alcohol.

Using the same apparatus and general method as was described in the previous experiment we added 34 Gm. of dichloroethyl ether to a refluxing solution of sodium tertiary butylate which had previously been prepared by dissolving 10.9 Gm. of sodium in 372 Gm. of tertiary butyl alcohol.

In this experiment the amount of condensate in the receiver was so trivial even after all of the dichloroethyl ether had been added that we used an additional 34 Gm. of this reactant. After the various purification steps had been carried out in the manner described in the previous experiment only 0.6 cc. of pure divinyl ether was obtained. The reasons for this poor result were not further investigated but it may be that the low solubility of sodium tertiary butylate in tertiary butyl alcohol as well as the low attainable refluxing temperature, *viz.*, 83–84° C., were contributing factors.

4. Fourth Method—Reaction between $\beta\beta'$-dichloroethyl ether and sodium tertiary amylate in tertiary amyl alcohol.

Dichloroethyl ether (90.8 Gm.) was added to a refluxing solution (115–120° C. oil-bath temperature) of sodium tertiary amylate prepared by dissolving 29.2 Gm. of sodium in 800 Gm. of tertiary amyl alcohol. The yield of practically pure divinyl ether, boiling point 28.3° to 29.5° C. amounted to 20 cc. or 34%.

After standing several days without any preservative this ether showed only 6–7 p. p. m. aldehyde when tested with the modified Nessler's reagent U. S. P. XI.

5. Fifth Method—Reaction between $\beta\beta'$-dichloroethyl ether and sodium tertiary hexylate in tertiary hexyl alcohol.

Dichloroethyl ether (63.3 Gm.) was added to a refluxing solution (oil-bath temperature 125–130° C.) of sodium tertiary hexylate prepared by dissolving 20.4 Gm. of sodium in 800 Gm. of tertiary hexyl alcohol. The yield of pure divinyl ether amounted to 8.5 cc. or 21%.

6. Sixth Method—Reaction between $\beta\beta'$-dichloroethyl ether and sodium 2-ethyl hexylate in 2-ethyl hexyl alcohol (octyl alcohol).

Dichloroethyl ether (45 Gm.) was added to a refluxing solution (oil-bath temperature 155–160° C.) of sodium 2-ethyl hexylate prepared by dissolving 14.5 Gm. of sodium in 256 Gm. of 2-ethyl hexyl alcohol. The yield of practically pure divinyl ether, boiling point 28–31° C. amounted to 10.5 cc. or 36%.

2.5 cc. of the divinyl ether thus prepared gave a yield of 7.6 Gm. of tetra bromo ethyl ether melting sharply at its recorded melting point, *viz.*, 64° C. This is 71% of the theoretical yield, and considering that there was an additional yield of less pure product and also many necessary losses of product it is reasonable to conclude that the divinyl ether used was practically pure.

CONCLUSIONS.

1. It has been shown that divinyl ether can be prepared in homogeneous reaction mixtures by the withdrawal of hydrogen chloride from $\beta\beta'$-dichloroethyl ether using either potassium hydroxide or sodium alcoholates when these alkaline reagents are dissolved in alcohols which do not participate in etherifications of the Williamson reaction type.

2. Suitable laboratory preparative methods for divinyl ether which involve only ordinary laboratory glass-ware and simple laboratory methods have been developed.

REFERENCES.

(1) Cretcher and Pittenger, *J. A. C. S.*, 47, 164, 1174 (1925).
(2) Hibbert, Perry and Taylor, *Ibid.*, 51, 1551 (1929).
(3) Ruigh and Major, *Ibid.*, 53, 2663 (1931).

THE HYDROLYSIS OF MENTHYL ACETATE AND ACETYLIZED PEPPERMINT OIL.*

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INTRODUCTION.

In the routine examination of commercial samples of peppermint oil several questions arose concerning the kinetics of the reaction in which the acetylized oil is hydrolyzed with an alcoholic solution of potassium hydroxide. Some work has been done on the determination of the reaction velocity between menthyl acetate and potassium hydroxide (1), but apparently no investigation has been made of the reaction rate between acetylized peppermint oil and potassium hydroxide. The complexity of the constitution of peppermint oil might lead to the immediate assumption that the reaction between acetylized oil and potassium hydroxide could not be of the second order. Observations, however, showed that the reaction rates of the hydrolysis of acetylized peppermint oil and of pure menthyl acetate agree well enough to assume that the reaction of the acetylized oil is of the second order. It must be remembered that some samples of oil will show larger amounts of a constitutent, probably resinified material, which may react with potassium hydroxide to change the value of the velocity constant.

This work represents the first of a series of experiments to determine the reaction rates of the hydrolysis of acetylized peppermint oil and of menthyl acetate by potassium hydroxide in alcoholic solution at various temperatures. For the work included in this report temperatures of 25° C., 30° C. and 35° C. were used. The purpose of the menthyl acetate was to provide a standard of comparison.

REAGENTS AND EXPERIMENTAL PROCEDURE.

Peppermint Oil.—The peppermint oil used in this work was a composite sample collected during the latter part of the 1934 season. Analysis of the oil gave the following constants: Optical rotation, $-22.6^{27^\circ}_{\mathrm{D}}$; esters, 9.66%; total menthol, 50.23%. From this sample a sufficient quantity of acetylized oil was prepared according to the procedure of the U. S. P. X in the monograph for peppermint oil.

Menthyl Acetate.—Menthol, U. S. P. X, was refluxed with fused sodium acetate and an excess of acetic anhydride, C.P., for one hour. After washing with sodium carbonate T.S. to remove excess acetic anhydride, and drying over fused calcium chloride, the product was distilled under reduced pressure. The following constants were obtained: B. p. 81.5–82.5° 4 mm.; optical rotation, $-72.9^{27^\circ}_{\mathrm{D}}$.

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* Scientific Section, A. Ph. A., Dallas meeting, 1936.

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