

[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK & CO., INC.]

THE PREPARATION AND PROPERTIES OF PURE DIVINYL ETHER

BY WILLIAM L. RUGH AND RANDOLPH T. MAJOR

RECEIVED MARCH 21, 1931

PUBLISHED JULY 8, 1931

The first recorded reference to divinyl ether occurs in a paper by Semmler¹ "On the Ethereal Oil of *Allium Ursinum L.*" The divinyl sulfide, which was obtained from the essential oil of this plant, when treated with silver oxide yielded a low-boiling, sulfur-free liquid, the boiling point of which was about 39°. Two determinations of the molecular weight corresponded with the calculated value for divinyl ether. Semmler did not further characterize this liquid.

An attempt to prepare divinyl ether by the exhaustive methylation of morpholine was made by Knorr and Matthes.² A few drops of liquid were obtained but the quantity was insufficient for either an analysis or a determination of its boiling point.

Cretcher, Koch and Pittenger³ attempted to prepare divinyl ether by the action of heated sodium hydroxide on β,β' -dichlorodiethyl ether. The reaction was carried out in an iron pot surmounted by a Crismer column. The distillate came over at 84–85°. From it they were able to isolate β -chloroethyl vinyl ether, 1,4-dioxane, acetaldehyde and a "divinyl ether" which boiled at 39°. The yield of material that boiled at 39° was 4.7% of the amount that would have been expected if the conversion of the β,β' -dichloroethyl ether into divinyl ether had been complete. These authors evidently abandoned the attempt to prepare pure divinyl ether since they gave no properties of their product except its boiling point. The acetaldehyde formed in this reaction amounted to twice the weight of the material that boiled at 39°.

Hibbert, Perry and Taylor⁴ modified the method of the previous authors. They replaced the Crismer column with a reflux condenser kept at 40°; they used potassium hydroxide rather than sodium hydroxide, added the β,β' -dichlorodiethyl ether in small portions and lastly increased the time of heating. They obtained a 54.9% yield of a "divinyl ether" which boiled at 34–5°. Presumably, further details are contained in Canadian Patent Application 350,357.⁵ On brominating the material that boiled at 34–5° these authors obtained a compound, tetrabromoethyl ether, which melted at 63–64° and was identical with Freundler's "tetrabromobutyraldehyde."⁶ This was shown by analysis and by a mixed melting point.

¹ Semmler, *Ann.*, **241**, 111–116 (1887).

² Knorr and Matthes, *Ber.*, **32**, 736 (1899).

³ Cretcher, Koch and Pittenger, *THIS JOURNAL*, **47**, 1175–1176 (1925).

⁴ Hibbert, Perry and Taylor, *ibid.*, **51**, 1551 (1929).

⁵ Hibbert, Canadian Patent 302,437, July 29, 1930.

⁶ Freundler, *Compt. rend.*, **140**, 794, 1693 (1905); *Bull. soc. chim.*, [4] **1**, 71 (1907).

We have continued the study of the reaction between β,β' -dichlorodiethyl ether and the corresponding iodo ether with heated alkalis. In confirmation of the work of Cretcher, Koch and Pittenger we have isolated acetaldehyde, β -chloroethyl vinyl ether and 1,4-dioxane as products of this reaction. We have found, however, that divinyl ether boils at $28.3 \pm 0.2^\circ$ at 760 mm. The small amount of "divinyl ether," b. p. 39° , obtained by these authors was presumably a mixture which they did not further investigate. In addition to these products we have found evidence of the presence of ethylene oxide among the substances formed in the reaction. Also, in our preliminary work the gaseous products of the reaction were investigated and the presence of hydrogen and traces of acetylene were demonstrated.

Although the melting points of both pure sodium and potassium hydroxides are above 300° , ordinary C. P. grades which contain water fuse at a temperature below that at which reaction between the alkali and the chloro ether takes place. The reaction was very slow at temperatures below 170° ; the most satisfactory temperatures were between 200 – 250° .

It was found that during the course of the reaction a crust of sodium or potassium chloride formed over the surface of the fused alkali. When the alkali was well stirred and the crust formation prevented, it was found that only traces of acetaldehyde were formed. Without stirring, the amount of aldehyde was generally two to three times the amount of the divinyl ether formed. There was also considerable gas evolved during the reaction. Analysis showed that the gas consisted mainly of hydrogen with some unsaturated gases including traces of acetylene.

The yield of divinyl ether was very markedly increased by passing a slow stream of ammonia gas through the reaction system. The ammonia may either act as a true catalyst for the reaction or it may increase the yield by inhibiting the decomposition of the divinyl ether formed. A further study is being made of the function of the ammonia in promoting the reaction.

Several other reactions for the preparation of divinyl ether were studied but no other satisfactory process was found.

The important physical and chemical properties of divinyl ether have been determined and apparently for the first time it has been analyzed.

When divinyl ether was catalytically reduced with hydrogen in the presence of a platinum catalyst a 15% yield of diethyl ether was recovered. In addition to this acetaldehyde was found in the reaction mixture. This was evidently formed by hydrolysis of the divinyl ether during the reduction. Although some ethyl alcohol may have been formed by reduction of more of the aldehyde this was not determined. On the other hand, the work of Vavon, Skita and Adams on the selective reduction of olefin and aldehyde groups has shown that a platinum catalyst without a pro-

moter such as iron is not a very effective catalyst for the reduction of aldehydes.⁷

A recent patent by Hibbert⁸ has described the polymerization of "divinyl ether" in the presence of benzoyl peroxide. We have found that only 5 to 25% of our divinyl ether was polymerized when it was treated according to the directions given in this patent. Polymerization is practically completely inhibited by minute traces of ammonia.

The reactions of divinyl ether with bromine have been studied. These will be discussed in a forthcoming paper.

Experimental Part

Preliminary Study of the Reaction between β,β' -Dichloroethyl Ether and Heated Caustic Alkalies.—Considerable time was spent in attempts to prepare divinyl ether by the action of potassium hydroxide on β,β' -dichlorodiethyl ether according to the method of Hibbert, Perry and Taylor.⁴ The apparatus used by these authors was later modified in most of our preliminary runs by the use of a nickel-lined copper autoclave of about 500-cc. capacity in place of a copper flask. The end of the condenser was connected through the top of the autoclave by means of a tightly fitting stuffing box packed with a mixture of asbestos and graphite. Provision was made for a gas inlet tube and a thermometer well. Ice water was circulated through the second condenser and the liquid products were collected in a flask cooled with either solid carbon dioxide and acetone or ice and hydrochloric acid mixtures.

According to the description given by these authors the copper reaction flask was "strongly heated with a Bunsen burner." In order to control the reaction more carefully, we carried out experiments over the temperature range of 150–300°. They also stated that "finely powdered caustic potash" was employed. The ordinary "C. P." grades of sodium or potassium hydroxide melt at about 140–160° depending upon the amount of water that they contain. Since these authors did not mention any particular drying of the caustic potash we assumed that their reaction mixture actually consisted of fused rather than powdered alkali. However, we varied the water content of the alkali both by the addition of water and by boiling off the excess water at slightly higher temperatures than that at which the reaction was to take place. A mixture of sodium and potassium hydroxides (and water) was also tried.

Throughout these preliminary experiments and also in later work we were never able to obtain any trace of either a compound or a true constant boiling mixture which boiled between thirty and forty degrees.

⁷ Tuley with Adams, *THIS JOURNAL*, **47**, 3061 (1925); Skita, *Ber.*, **48**, 1685 (1915); Vavon, *Compt. rend.*, **154**, 359 (1912).

⁸ Hibbert, Canadian Patent, 302,437, July 29, 1930.

It was found that a considerable amount of gas was evolved during the reaction. When about eight drops of β,β' -dichlorodiethyl ether was added per minute, the flow of gas varied from 5 cc. per minute at 200° to about 65 cc. at 280°.

A qualitative test with ammoniacal cuprous chloride gave a small quantity of a red precipitate which showed the presence of a small amount of acetylene. The gas also gave a strong positive test for hydrogen with Pereira's test,⁹ using sodium tungstate, acetic acid and palladous chloride.

In most of the preliminary runs a small amount of material that boiled between 20 and 30° was obtained. This material contained a large amount of acetaldehyde. We also found 1,4-dioxane and β -chloroethyl vinyl ether in the distillate, in confirmation of the work of Cretcher, Koch and Pittenger.³ However, we were unable to obtain the "divinyl ether" whose boiling point they gave as 39°.

Since they made no further study of the properties of their "divinyl ether," b. p. 39°, we presume that they abandoned further study of the compound due to the small yield obtained. We were thus forced to the conclusion that if divinyl ether was a product of this reaction it must be contained in the fraction boiling between 20 and 30°.

The low-boiling distillate from five runs using a total of about 400 g. of the chloro ether was collected and amounted to 123.5 g. This material was treated successively with solutions of sodium bisulfite, dilute alkali, sodium carbonate and hydroxylamine hydrochloride, washed several times with water, and finally dried over calcium chloride. The aldehyde-free material from this treatment weighed 37.7 g. After two fractionations, the largest cut weighing 15.9 g. boiled at 27–29° (uncorr.). The method of purification was later improved as follows: the crude low-boiling distillate was shaken with a dilute solution of ammonia, allowed to stand in the ice box for several hours in contact with an excess of the dilute ammonia and finally washed several times with water. After it had been dried over calcium chloride and then sodium, it was distilled through a Clarke column; the fraction which boiled at 28.3 to 28.5° (corr.) at 768 mm. was pure divinyl ether. The corrected boiling point at 760 mm. was 28.3 \pm 0.2° (obtained on another 250-g. sample).

Properties of Divinyl Ether.—Divinyl ether rapidly decolorized bromine in carbon tetrachloride; it was also readily oxidized by an aqueous solution of potassium permanganate. The absence of any acetylenic linkage was shown by a negative test with ammoniacal cuprous chloride. Concentrated sulfuric acid reacted violently with it to give a black tarry resin and some free aldehyde. Cold concentrated hydrochloric acid gave a yellow color with divinyl ether and the odor of acetaldehyde was apparent. Dilute hydrochloric acid hydrolyzed divinyl ether rapidly to acetaldehyde (confirmed by the *p*-nitrophenylhydrazone).

A solution of *p*-nitrophenylhydrazine in 50% acetic acid to which a few drops of

⁹ Pereira, *Chem. Abstracts*, 7, 3284 (1913).

dilute hydrochloric acid had been added reacted rapidly with divinyl ether and gave the *p*-nitrophenylhydrazone of acetaldehyde, m. p. 128.5–129°. A mixed melting point with some material prepared directly from acetaldehyde also melted at 128.5–129°.

In the absence of hydrochloric acid, divinyl ether did not react with *p*-nitrophenylhydrazine in 50% acetic acid after standing for thirty minutes at room temperature.

Divinyl ether gave an immediate precipitate of iodoform when the test was applied at 0°, using the procedure of Mulliken.¹⁰

Tollens' reagent showed no darkening with the ether within half an hour when the mixture was kept cold. Schiff's reagent, however, gradually developed a pink color, due presumably to the acetaldehyde which was liberated by hydrolysis in the presence of the free acid.

Pure divinyl ether boiled at 28.3° = 0.2° (760 mm.); mol. wt. calcd. for C₄H₆O, 70.05; found (Victor Meyer Method): 74.43, 71.15; d_{20}^{20} 0.774; d_4^{20} 0.773; n_D^{20} 1.3989; mol. refraction, calcd. for C₄H₆O (by Lorentz-Lorenz formula),¹¹ 21.38; found, 21.93.

Analysis.—The carbon and hydrogen analyses were performed in a modification of Reid's apparatus (Fig. 2).¹² Owing to the explosive nature of certain mixtures of divinyl ether and air, the inner tube of the apparatus was a 1-mm. Pyrex capillary tube which was loosely plugged at intervals with glass wool. This capillary tube extended to within a half centimeter of the copper oxide. A metallic wool such as silver would have probably been more efficient to prevent "backfires" because of its greater conductivity of heat. A small bulb of about 0.5-cc. capacity was blown in the capillary just below the "sample tube." Before breaking the sample bulb the lower part of the apparatus was chilled with a freezing mixture.

Anal. Calcd. for C₄H₆O: C, 68.52; H, 8.64. Found: C, 67.78, 68.44; H, 8.61, 8.61.

Reduction of Divinyl Ether.—Half a gram of a platinum oxide catalyst¹³ in 75 cc. of redistilled *n*-butyl alcohol was reduced in a Burgess-Parr reduction apparatus.¹⁴ A sealed ampoule containing 12.52 g. of divinyl ether was then placed in the reductor bottle. After the preliminary evacuation of the bottle, the ampoule was broken and hydrogen admitted to the system. Reduction stopped when about half the theoretical amount of hydrogen had been absorbed. The bottle and its contents were cooled in a mixture of solid carbon dioxide and acetone and opened. One-tenth of a gram of catalyst and 100 cc. more of *n*-butyl alcohol were added and the reduction continued. After twenty-four hours 0.3 g. more of the catalyst was added as before. Reduction proceeded rapidly until about the theoretical amount of hydrogen had been absorbed, when absorption abruptly stopped. However, since the total reduction required eighty-eight hours, presumably some hydrogen was lost through leakage.

The butyl alcohol solution was filtered and distilled through a Clarke column. The first fraction, which boiled between 30 and 70° (practically all between 30 and 40°), weighed 4.9 g. An odor of acetaldehyde was noticeable. By treatment of 0.11 g. of this fraction with *p*-nitrophenylhydrazine in dilute acetic acid, 0.029 g. of crude acetaldehyde *p*-nitrophenylhydrazone (m. p. 124–125°) was obtained. The fraction of b. p. 30–70°, therefore, contained about 6.4% of acetaldehyde. This fraction was then treated with dilute hydrochloric acid for half an hour, the acid neutralized with sodium

¹⁰ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 166.

¹¹ Landolt-Brönstein, "Tabellen," Julius Springer, Berlin, 1912, p. 1039.

¹² Reid, THIS JOURNAL, 34, 1033 (1912).

¹³ Adams and Shriner, *ibid.*, 45, 2171 (1923).

¹⁴ Manufactured by the Burgess-Parr Company, Moline, Ill.

hydroxide, the ether layer separated, dried first over anhydrous sodium carbonate then over sodium and distilled. All this liquid boiled between 34.6–35.2° at 767 mm. and the distillate weighed 2.02 g. The refractive index was found to be $n_D^{17.1}$ 1.3540.¹⁵ The yield of pure ethyl ether was thus 15.2%. Considerable loss of the product occurred during the processes of purification.

Polymerization of Divinyl Ether.—A summary of the results obtained during attempts to polymerize divinyl ether is given in Table I. The general procedure was to add the benzoyl peroxide (recrystallized, m. p. 106–107°) to a cold dry bomb tube, then add the divinyl ether and seal. The tubes were then heated in a Freas electric oven for the period stated, cooled and opened. The polymer together with the unpolymerized divinyl ether was obtained on opening the tubes. The procedure used was that given by Hibbert in a recent patent.⁵

TABLE I
POLYMERIZATION OF DIVINYL ETHER

Run	Divinyl ether, g.	Benzoyl peroxide, mg.	Temp., °C.	Time of heating, hours	NH ₃	Product, g.	Yield of polymer, %
1	5	25	90–96	24	Trace	0.073	0.96
2	5	25	90–96	24	Trace	...	2
3	5	50 ^a	95–100 ^b	25	...	1.28	24.6
4	2.5	12.5	92–94	24	...	0.32	12.4
5	2.5	25 ^a	92–94	24	...	0.19	6.4
6	2.5	12.5	91–93	24.5	...	0.199	7.5
7	2	12.5	91–93	24.5	Trace	0.012	0
8	2.5	12.5	91–93	24.5	...	0.527	20.6

^a The ratio of benzoyl peroxide to divinyl ether was twice that given in the patent of Hibbert. ^b The oven overheated for a short time to about 130° at the beginning of this run.

Ethylene Oxide as a Product of the Reaction.—Ethylene oxide was presumed to be a product of the reaction because the low-boiling fraction (15–25°) of these runs was almost completely removed by treatment with ammonia. When efficient stirring of the potassium hydroxide was maintained, very little acetaldehyde was found. Distillation of the product under these conditions showed that 20% of the material came over below 27° during the first fractionation.

To confirm the presence of ethylene oxide the test given by Mulliken was applied in conjunction with several blanks.¹⁶ In each test about 1.5 cc. of a saturated solution of magnesium chloride and 0.1–0.3 cc. of the material to be tested was placed in a tightly stoppered 7.6-cm. test-tube. These were kept at 0° for six hours and then allowed to stand at room temperature.

¹⁵ "International Critical Tables," McGraw-Hill Book Co., New York, 1930, Vol. VII, p. 36, gives $n_D^{17.1}$ 1.35424.

¹⁶ Ref. 10, p. 160.

- | | |
|---------------------------|-------------------------------------|
| 1. Acetaldehyde | No precipitate after 60 hours |
| 2. Pure divinyl ether | No precipitate after 60 hours |
| 3. Fraction, b. p. 15–27° | Heavy precipitate after 24 hours |
| 4. Pure ethylene oxide | Heavy precipitate after 12–24 hours |

Reaction between β,β' -Diiododiethyl Ether and Fused Potassium Hydroxide.—To 150 g. of potassium hydroxide in the reaction vessel was added 100 g. of β,β' -diiododiethyl ether¹⁷ during the course of two hours and forty-five minutes. The autoclave was kept at 190–200°. The distillate amounted to 16.7 g. and contained considerable acetaldehyde. After the treatment with ammonia, 6.7 g. of material was left of which 3.3 g. boiled between 23 and 28° (practically all at 27–28° uncorr.). The yield of divinyl ether was thus 15%.

Ammonia as a Catalyst.—The run with the diiodo ether was repeated under practically the same conditions as before except that a slow stream of dry ammonia was ran through the system. A smaller amount (75 g.) of the ether was used. The yield of divinyl ether was 5.6 g. or 34%. The use of ammonia as a catalyst increased the yield slightly more than 120%.

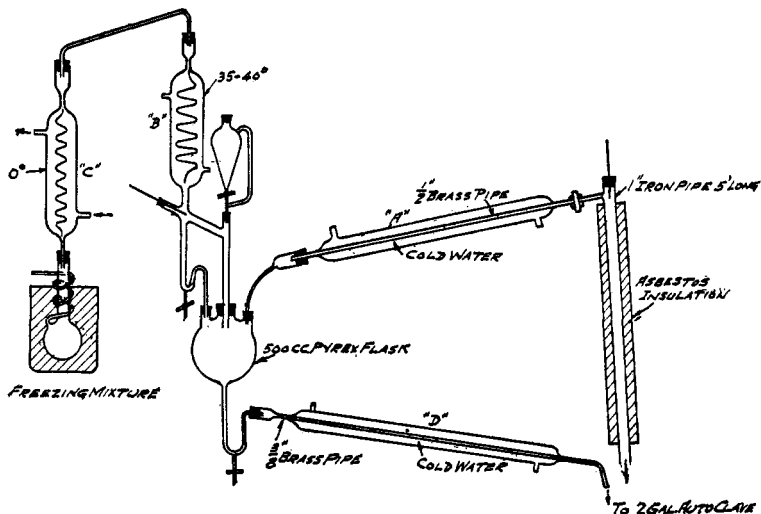


Fig. 1.

Preparation of Divinyl Ether when the Molten Alkali was Stirred without the Use of Gaseous Ammonia.—The apparatus was set up as shown in Fig. 1. A charge of 7 kg. of technical lump potassium hydroxide was placed in the autoclave. *Efficient stirring of the molten alkali was found desirable.* For this reason the level of the fused alkali was well below the upper arm of the stirrer blades. If this point was disregarded, a crust of potassium chloride, etc., formed over the surface of the fused alkali. This resulted in reduced yields, production of large amounts of acetaldehyde and a very marked slowing down of the speed of reaction. When efficient stirring was maintained, practically no acetaldehyde was formed.

In the preliminary runs in which the original small scale apparatus was used without stirring, the amount of acetaldehyde formed was generally about twice the yield of divinyl ether. A run was made in the new apparatus with efficient stirring but without

¹⁷ Gibson and Johnson, *J. Chem. Soc.*, 2525 (1930).

the use of ammonia. From 923 g. of dichlorodiethyl ether was obtained 101.5 g. of distillate of which 5 g. was in an aqueous layer. Practically no aldehyde was present as was shown by tests with Tollens' and Schiff's reagents and with *p*-nitrophenylhydrazine. It may be noted here that whereas acetaldehyde formed the *p*-nitrophenylhydrazone with the hydrazine in dilute acetic acid solutions almost immediately, divinyl ether gave the hydrazone only very slowly after long standing.

Ethylene oxide was, however, a by-product of this run as shown by the previously described test.

From this reaction, 59.8 g. of material was obtained, b. p. 20–33°. This corresponds to a yield of 13.3% if this were all divinyl ether. Due to accidental loss of one of the fractions, the product was not purified by treatment with ammonia.

The reaction took place best when the temperature of the fused alkali was kept at about 200–240°; lower temperatures result in slowing up the reaction. The effect of temperatures above 250° was not determined in this apparatus.

Samples of the gas from this reaction were collected over water and then analyzed. The flow of gas varied from 400 to 500 cc. per minute and a total of four liters of gas was taken at intervals during the reaction. The analyses were made over water with a Hempel apparatus. The following results were obtained

Unsaturated	15.7%	(absorption in bromine water)
Oxygen	1.0%	(absorption in alkaline pyrogallol)
Hydrogen	78.5%	(combustion over copper oxide at 270°)
Residue	4.7%	
Total	99.9%	

The residual gas after the removal of the unsaturated gases, oxygen and hydrogen was analyzed for methane and ethane in a mercury-filled combustion pipet. Less than 0.5% of saturated hydrocarbons was found in the total sample. The 4.7% residue was thus principally nitrogen.

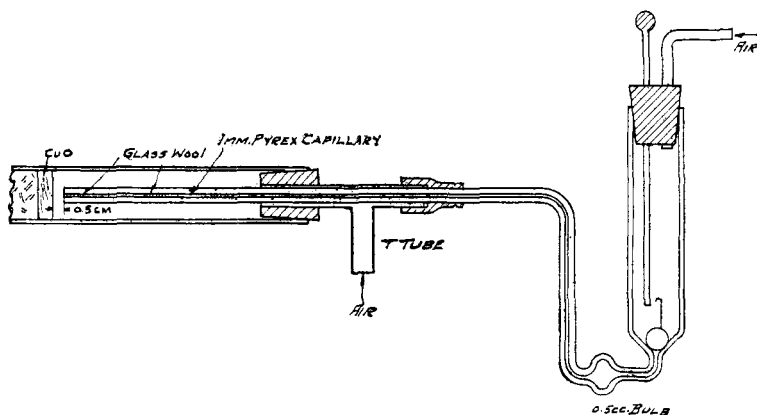


Fig. 2.

The unsaturated gas probably contained some divinyl ether since the condenser for the liquid products of the reaction was cooled only to about -15° during this run. A trace of acetylene in the gas was shown to be present by the small amount of red precipitate which was formed when the gas was passed through an ammoniacal solution of cuprous chloride.

Reaction in the Presence of Gaseous Ammonia.—When a slow stream of gaseous ammonia was passed through the system, the yield of divinyl ether was considerably increased. Using the new apparatus, the autoclave was first heated to about 230° and ammonia gas passed in through the gas inlet tube at about 1 to 3 bubbles per second. The addition of the β,β' -dichlorodiethyl ether was so regulated that condenser "B" did not become choked with the refluxing liquid. From time to time it was necessary to withdraw from the trap the excess of water, dioxane and β -chloroethyl vinyl ether which otherwise would have choked the condenser "B." The apparatus had a capacity of 1.5–2 kg. of the dichloro ether in eight hours. The capacity could have been increased by the employment of more efficient condensers. Condenser "B" in particular, being of spiral form, was rather readily choked with the refluxing liquid.

From 1850 g. of the dichloro ether in ten hours was obtained 272.8 g. of organic distillate. On fractionation, 192.5 g. of crude divinyl ether, b. p. 26.3–30° (uncorr.), was collected. The yield was thus 21%. From four runs using a total of 4750 g. of the chloro ether was obtained 478 g. of crude divinyl ether (b. p. 25–30°), or a yield of 20.3%. When the yield was corrected for losses due to a breakdown and for withdrawals of β -chloroethyl vinyl ether, the yield was about 25%.¹⁸

In comparing these results with the yield obtained without the use of ammonia (13.3%) it must be remembered that this yield was of relatively impure divinyl ether since it had not been purified by treatment with aqueous ammonia. In the runs using gaseous ammonia the purification consisted in washing the crude distillate several times with water, drying over calcium chloride and distilling through a Clarke column.

In order to remove all traces of ammonia, the fraction of b. p. 27–29° was washed once or twice with ice water (testing the wash water with methyl orange), dried over calcium chloride, then over sodium and redistilled.

Reaction between β,β' -Dihalogen Diethyl Ether and Sodamide.—The copper autoclave of the apparatus used in the preliminary runs was replaced by a 1-liter 3-necked distilling flask equipped with a mercury-sealed stirrer. In the flask were placed 300 cc. of dry xylene and 70 g. of very finely powdered sieved sodamide. The mixture was heated to the boiling point of the xylene and 100 g. of dichlorodiethyl ether run in during the course of four hours. Toward the end of the reaction, an additional 20 g. of fresh sodamide was added.

The product, collected in a receiver cooled with a solid carbon dioxide–acetone mixture, consisted mostly of liquid ammonia. About 1.5 g. of crude divinyl ether was obtained on fractionating this distillate; yield, 3%.

A run was made in which 50 g. of β,β' -diiododiethyl ether was used. The yield from this reaction was likewise very poor.

Action of Tertiary Amines on β,β' -Dihalogen Diethyl Ethers.— β,β' -Dichloro diethyl ether (5 g.) was refluxed with 15 g. of dimethylaniline for two hours. No reaction took place as was shown by the absence of any precipitate on the addition of dry ether.

The β,β' -diiododiethyl ether when refluxed for five minutes with dimethylaniline gave a voluminous precipitate. When recrystallized from alcohol it formed shimmering white leaflets of m. p. 220–230° (decomp.).

Anal. Calcd. for $C_{20}H_{30}I_2N_2O_2$: C, 41.28; H, 5.33; N, 4.93. Found: C, 41.47, 41.43; H, 5.53, 5.60; N, 5.12.

The material was thus the diiodide of bis- β,β' -phenyldimethylaminoethyl ether.

A mixture of 25 g. of the chloro ether and 100 g. of pure synthetic quinoline was gradually heated up to the boiling point and then refluxed for several hours. No trace

¹⁸ The best yield obtained, using a solid carbon dioxide–acetone mixture to cool the receiving flask, was 38%.

of divinyl ether was obtained. The reaction mixture solidified to a tarry mass when it was cooled.

Attempts to Dehydrate β,β' -Dihydroxydiethyl Ether.—Activated alumina was heated in the autoclave at 200° and β,β' -dihydroxydiethyl ether slowly added. No divinyl ether was obtained, the products being mainly aldehydes.

Phosphorus pentoxide reacted violently with the β,β' -dihydroxydiethyl ether and gave a tarry gum. The reaction was tried with xylene as a diluent but no divinyl ether was obtained.

Soda Lime and β,β' -Dichlorodiethyl Ether.—Several runs were made in an attempt to prepare divinyl ether by passing the vapor of the chloro ether over soda lime at 250–300°. Aldehydes were obtained but no divinyl ether.

We take pleasure in acknowledging the assistance of Doctor William Engels in the design of the apparatus for the preparation of divinyl ether, and of Mr. Douglass Hayman for the analysis of the diiodide of bis- β,β' -phenyldimethylaminoethyl ether.

Summary

1. Several methods for the preparation of divinyl ether have been studied, the most successful being the reaction of β,β' -dichlorodiethyl ether and caustic alkali in the presence of ammonia.

2. Divinyl ether has been prepared, analyzed and a number of its physical and chemical properties determined.

3. Pure divinyl ether was partially polymerized by the method described in a recent patent.^b Traces of ammonia inhibited this polymerization.

4. Diethyl ether has been formed by the catalytic reduction of divinyl ether.

5. In addition to divinyl ether, the following substances were formed during the reaction between β,β' -dichloroethyl ether and caustic alkali: hydrogen, acetylene, ethylene oxide, β -chloroethyl vinyl ether, 1,4-dioxane and acetaldehyde.

RAHWAY, NEW JERSEY