which exists between the class of polypeptide hydantoins and the closely related class of dioxypyrimidines, since the latter under similar conditions react to give mixtures of N-1 and N-3 substitution products.

The fact that geometrical isomers have been found to exist is of especial importance because it would seem to indicate the possibility of a certain rigidity in the configuration of the hydantoin molecule. Previous to this time the assumption has been made that the mobility of the atoms which go to make up the molecule of tautomeric substances may be regarded as operating against the fixed arrangement of parts which is generally presupposed in order to account for the phenomena of optical and geometrical isomerism.

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[Contribution from the Chemical Laboratory of the University of Illinois]

PREPARATION OF ABSOLUTE ALCOHOL WITH CALCIUM CHLORIDE AND LIME

By William A. Noyes

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Beilstein's "Handbuch der Organischen Chemie" states that absolute alcohol is prepared on a large scale by the use of calcium chloride but I have failed to find details anywhere in the literature. The statement is also made that alcohol combines with calcium chloride and that a high temperature is required to expel the last of the alcohol from the compound formed.

A somewhat extended study of the relations involved has established the following facts.

1. From strong alcohol containing somewhat more than 1 mole of calcium chloride (111 parts) for 1 mole of water (18 parts), alcohol of 99.5% concentration or stronger, may be distilled.

2. On concentration of such a solution a solid alcoholate, not a hydrate, begins to separate when the boiling point reaches 95–100° and there is an equilibrium between the alcoholate and hydrate present. A quite high temperature is required to expel the alcohol from the solid alcoholate.

3. The hydrate of calcium chloride containing 4.5 moles of water (80 parts) for 1 mole of calcium chloride (111 parts) boils at 140° and from such a solution the alcohol may be distilled completely with a strength of 90% or greater. The solution of calcium chloride of this composition is liquid at 140° but solidifies on cooling.

4. Successive distillations of alcohol containing 80 g. of calcium chloride per liter increase the strength of the alcohol approximately as follows, by weight.

Change % From	Change % To	Increase in strength	Change % From	Change % To	Increase in strength
83.0	91.5	8.50	97.0	98.4	1.40
90.0	94.5	4.30	98.0	98.8	0.80
93.0	96.3	3.25	98.5	99.0	0.50
95.0	97.25	2.25	99.0	99.35	0.35
96.0	98.0	2.00	99.25	99.50	0.25

These principles may be applied for the preparation of alcohol of 99.0 to 99.6% by weight, by means of the apparatus shown in Fig. 1. This apparatus may be constructed of galvanized iron.

A is a condensing worm, which has 10 turns of block-tin pipe 13 mm. in external diameter, the coil being 7 cm. in external diameter and 20 cm. high. Alcohol may be condensed at the rate of 6 or 7 liters per hour with such a coil. B is a condenser, shown in cross-section at the side of the figure, designed to serve as a reflux condenser during a part of the operation. Since the compartment LD is filled with alcohol vapor during the distillation, as cold water is passed through B, alcohol condenses on the under side of the sheet metal top and runs back into this compartment. C is an opening through which the anhydrous calcium chloride is introduced. D is a diaphragm to prevent spray from passing into the condenser. E is a shelf to hold the calcium chloride until it dissolves. At F there are 18 holes, 6 mm. in diameter, through which the vapor of the alcohol passes upward from below and through which the calcium chloride solution drains downward when the apparatus cools. G is a shelf 1 cm. below E. It is turned upward to a height of 15 mm. at the edge so that the solution above E cannot run away so long as alcohol vapor is passing upward, thus securing a quantity of alcohol sufficient for the solution of the calcium chloride. The shelves H, H′, etc., are turned upward to a height of 15 mm. at their edges, so that when the calcium chloride solution drains downward to the level of the dotted lines, on cooling, about 500 cc. of the solution will remain on each shelf. These shelves are 50 mm. apart. Half way between each pair are the shelves I, I′, etc., with edges turned downward 20 mm. During the passage of the vapors upward the greater part of the calcium chloride solution will be on top of these shelves and will be continually agitated by the passage of the vapors. M is a brass tube to which a rubber tube and funnel are attached for the introduction of alcohol and removal of spent calcium chloride. As a matter of safety this should be replaced by a brass tube reaching to the top of the apparatus and a stopcock for the removal of the calcium chloride.

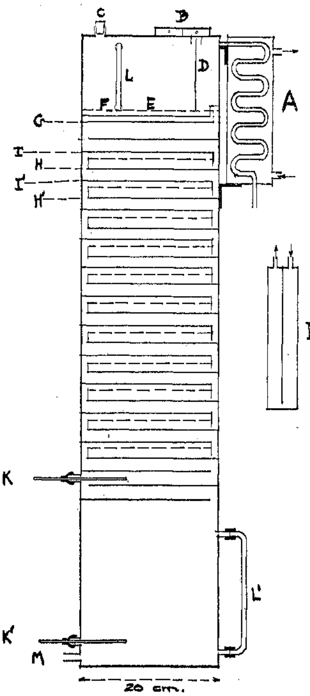

Fig. 1.

If the calcium chloride available is not entirely anhydrous, it should be heated to 250–300° until no water remains. We have found a heavy iron mortar useful for this purpose but have used, in the later experiments, a commercial calcium chloride which does not require heating.

In using the apparatus at first, 200 g. of calcium chloride is placed in the top, 1 liter of 92–93% alcohol is added in the top and 4–5 liters in the bottom. Alcohol is then distilled from below until 200–300 cc. has been condensed by the reflux condenser, B, and 500–700 cc. has been collected at the bottom of the condenser, A, the apparatus being heated by a small, efficient gas stove which will distil 2500 cc. in 20–25 minutes, when the condenser B is not used. The apparatus is then cooled for a moment and the solution in LD is allowed to run back to the compartment below. The gage L enables the operator to know how much of the solution has collected in the top compartment and when it has drained back. The removal of the solution may sometimes be hastened to advantage by wiping the outside of the can with a cold, wet sponge or cloth; 200 g. more of calcium chloride is then added in the top and more alcohol, as may be necessary, in the bottom and the operation is repeated until a distillate of 99% or above is obtained. Enough alcohol must be condensed and returned each time so that undissolved calcium chloride does not accumulate in the top; 200 g. of calcium chloride is again placed in the top and 2500 cc. of alcohol distilled and collected. This may be repeated 3 or 4 times, after which it may be advisable to use 200 g. extra of the calcium chloride and return 1000 cc. of the distillate as in the earlier part of the operation.

While the 2500 cc. lots are being collected it is usually unnecessary to condense more than a very little alcohol by means of the condenser B. Only enough to secure the solution of the calcium chloride should be condensed.

The first use of the apparatus, as described, gave in the 7 preliminary distillations, successively, alcohol of 97.33, 97.97, 98.14, 98.65, 98.74, 99.06 and 99.14% concentration; it then gave 4 lots of 2500 cc., each, of 99.43, 99.51, 99.42 and 99.08%. In another case where the preliminary distillations had brought the alcohol to 99.33%, 4 distillations gave 2500 cc. each of 99.54, 99.38, 99.28 and 99.13% strength. In another case in which 200 g. extra of calcium chloride was used after every 2 lots of 2500 cc., with the return of 1000 cc., the concentrations of the successive distillates were 99.56, 99.35, 99.47, 99.29, 99.35 and 99.31%. During the distillations enough 92–93% alcohol is added in the bottom so that the temperature of the solution does not rise above 90°. After distilling 10 liters the distillation is continued until the thermometer K′ registers 95°.

During this process, as last described, 1000 g. of calcium chloride will have been used; 400–500 cc. of water is then added, the calcium chloride having retained about 600 cc. of water from the alcohol. The distillation is further continued until the thermometer K′ registers 125° to 130° and the thermometer K about 100°. The solution in the bottom will then be free from alcohol and is drawn off. More alcohol is then added and the operation continued, after using 200–400 g. extra of calcium chloride, to bring the distillate back to the desired strength.

From the aqueous solution of calcium chloride drawn off, anhydrous chloride may, of course, be recovered, but as the cost of the chloride used is equivalent to only 3 or 4 cents per liter of 99% alcohol obtained, this is hardly profitable in the ordinary laboratory.

By increasing the number of shelves or by turning the shelves H, H′, etc. up 20 or 25 mm. to increase their capacity, it should be possible to increase to 99.5% the strength of the alcohol secured or to lessen the amount of calcium chloride necessary to give this strength. The apparatus described is the most efficient of half-a-dozen forms which have been made and tried.

Dehydration of Alcohol with Lime.—The method described above for removing a large part of the water from alcohol has the advantage that it is rapid and that practically all of the alcohol is recovered. For the direct dehydration of 92% alcohol with lime it has been found best, in this Laboratory, to place 8 liters of alcohol and 2200 g. of lime in a 12-liter flask, connect with a reflux condenser, heat to boiling on a steam-cone and allow the mixture to react overnight. The heat of the reaction will keep the alcohol boiling for some time and on the following morning the distillate will have a strength of 99.6 to 99.7%. Even after long heating on the steam-cone the lime will retain 7 or 8% of the alcohol used and the loss may be very much greater if a large excess of lime is used. W. H. Warren[1] reports a loss of 33% under conditions which he recommends.

For the preparation of nearly absolute alcohol from alcohol of 99% obtained by the use of calcium chloride, the apparatus shown in Fig. 2 is useful.

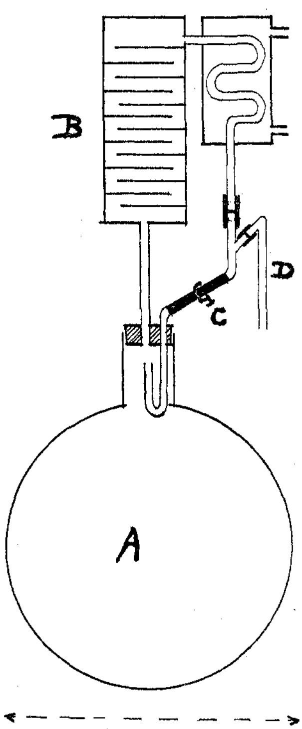

Fig. 2.

A is a 12-liter flask; B is a trap to prevent lime from being carried over mechanically with the alcohol vapor. It is now thought that so elaborate a trap is not needed (see below). When the pinchcock on the rubber tube at C is open, the condensed alcohol returns to the flask, giving the effect of a reflux condenser. When the pinchcock is closed, the condensed alcohol will pass through D and may be collected.

Ten liters of 99% alcohol and 400 g. of lime, after refluxing for 20–40 hours, will give a distillate of 99.9% concentration or stronger. The lime should be powdered and if the alcohol is stronger than 99% only about 50% in excess of the theoretical amount of lime should be used. The loss of alcohol under these conditions should not exceed 1 to 2%.

The distillate of very nearly absolute alcohol is always turbid. It was thought at first that lime was carried over mechanically, but the very effective trap shown in the figure failed to prevent the turbidity, and I have learned that the same observation has been made by a number of other chemists, though I have found no mention of the phenomenon in the literature. In one case 10 liters of 99.74% alcohol was heated overnight with 250 g. of lime. Three successive portions of

[1] Warren, This Journal, **32**, 700 (1910).

2500 cc. each were 99.92, 99.98 and 99.99% strong and contained, as shown by titration with standard acid, 5.0, 12.0, and 22.5 mg. of calcium per liter, respectively. One hundred cc. of the last gave, on evaporation in an open dish, 6.2 mg. of calcium carbonate, as compared with 6.4 mg. calculated. Redistillation of the turbid alcohol gives a clear distillate of unchanged strength, if exposure to the air is avoided.

It seems probable that the calcium volatilizes as calcium ethylate and that this is converted to the hydroxide by a very slight exposure to the air. Only 0.003% of water would be required for the sample which contained most calcium.

For the practical laboratory preparation of absolute alcohol, in case the apparatus for the use of calcium chloride is not available the best method is probably to put 10 liters of 92% alcohol and 2000 g. of good lime in the 12-liter flask of the apparatus last described. After refluxing for 24 hours, alcohol of 99% concentration can be obtained, with a loss of only about 4% of alcohol actually present. The 99% of alcohol obtained in this way, or that obtained by calcium choride, is then best refluxed for 24 hours with 350 g. of good lime, which should bring it to 99.7%, or higher. It will probably now be turbid. It is then mixed with about 50% more than the required amount of calcium oxide prepared by heating hydrated lime[2] as described by Danner and Hildebrand.[3] Anhydrous calcium chloride amounting to 10 or 15% of the lime used should be added and the alcohol distilled after refluxing overnight. This should give clear alcohol of at least 99.9% concentration.

Dehydration of Alcohol with Sodium.—Some chemists seem to think that small amounts of water may be removed from strong alcohol by sodium. Such a method is objectionable for two reasons. Sodium ethylate, alcohol, water and sodium hydroxide form an equilibrium such that some water will always pass over with the alcohol. It would seem that the hydrogen ionizations of alcohol and water are somewhat of the same order, that of water being greater.[3] Thus, 510 g. of 99.66% alcohol with 5 g. of sodium (calc. 2.2 g.) gave alcohol of only 99.88% concentration. Again, 552 g. of 98.79% alcohol with 11.25 g. of sodium (calc., 8.52 g.) gave a solution which could not be distilled from a water-bath. Distilled over a free flame, this gave 376 g. of 99.22% and 58 g. of 99.45% alcohol. Besides its inefficient conversion, sodium ethylate is very sensitive to oxidiation on exposure to the air and an impure alcohol may result from its use.

Summary

An apparatus is described by means of which alcohol of 99.0–99.5% concentration may be prepared rapidly with calcium chloride.

[2] The hydration equivalent should be determined by adding 1 cc. of water to 1 g. of the lime and heating to 150° in an air-bath, the crucible being covered with a watch glass.

[3] See Danner and Hildebrand, This Journal, **44**, 2824 (1922).

An apparatus is also described for preparing absolute alcohol with lime.

When absolute alcohol is distilled from an excess of lime a little calcium passes over, probably as calcium ethylate.

Metallic sodium is not suitable for the preparation of absolute alcohol.

URBANA, ILLINOIS

NEW BOOKS

Aus meinem Leben (Out of my Life). By EMIL FISCHER. Julius Springer, Berlin, 1922. 201 pp. 3 portraits. 16 × 23.5 cm. Price M 300, bound.

In his "Reminiscences of Departed Friends" A. W. Hofmann has truly said: "The history of a scholar is the history of his specialty."

In 1922, the Julius Springer Press of Berlin published a two-hundred page book of reminiscences of Emil Fischer, edited by M. Bergmann. These were written by Fischer in 1918, a year so momentous for Germany, while he was on a trip for his health to Locano and Karlsbad, and later were to have been amplified into a complete autobiography. This intention he was unable to carry out and the manuscript, as thus edited by Bergmann, is the parting greeting to his friends and to the world of a man who had no peer in the field of organic chemistry, and who died as he had lived, unselfishly and with the kindliest of feeling towards all, but saddened in his last days by the personal losses which the war had caused in his own family and by the almost complete disruption of a lifetime's investigations, which were continuing to bear such a rich harvest for science.

Broken as he was in spirit and body, for already the seeds of the fatal malady which was soon to cause his death were at work, it seems strange that he could concentrate on these reminiscences all that fascinating power of intellect and keenness of humor, which in his younger days he possessed to so marked a degree. The explanation may perhaps be found in the words of Kussmaul:

> "Musst du Gram im Herzen tragen
> Und des Alters Schwere Last
> Rufe dir aus jüngeren Tagen
> Die Errinnerung zu Gast!"

The first chapter of the text describes Emil Fischer's early youth and introduces the reader to his parents. Born at Euskirchen, the son of a well-to-do merchant, Emil Fischer passed a happy childhood in the joyous Rhineland. After passing the examination preliminary to entering the University, following out the desire of his father, he began, with much misgiving, to study for the career of a merchant. Apprenticed to his brother-in-law, Friedrichs, a successful lumber merchant of a neighboring town, after a few months of running errands, sealing and stamping envelopes, Fischer became convinced that the life of a merchant had no at-