Analyses. Calc. for $C_{21}H_{30}O_2N_2.2HCl$: N, 6.75; Cl, 17.08. Found: N, 6.96; Cl, 16.96.

Neither the *l*- base nor any of its salts could be obtained crystalline.

d-N-**Methyl-O-Ethyl-dihydrocupreicinol.**—*d*-O-Ethyl-dihydrocupreicinol hydrate was treated in dry acetone with an equivalent of methyl iodide. The N-methyl hydriodide which separated as minute rosets and prismatic needles was converted into the base by addition of sodium carbonate to its aqueous solution. Recrystallized from 50% alcohol, it formed rosets of long, narrow, glistening platelets which melted slowly at 136.5–137.0° with slight preliminary softening, giving $[\alpha]_D^{26.5}$ + 88.2° in absolute alcohol, $c = 0.993$, and greatly resembled the corresponding dihydroquinicinol base in properties and reactions, except for a slightly greater solubility in organic solvents.

Analyses. Calc. for $C_{22}H_{32}O_2N_2$: C, 74.10; H, 9.05; N, 7.87. Found: C, 74.16; H, 8.93; N, 8.64.

d-N,O-**Diethyl-dihydrocupreicinol.**—Equimolecular amounts of the base and ethyl iodide were allowed to react in dry acetone, the hydriodide of the diethyl compound separating as sheaves of delicate needles. The base, obtained from the salt as in the preceding case, crystallized on adding a little ether and allowing this to evaporate. It was dissolved in hot 70% alcohol, cooled, and treated with water until just turbid, separating slowly when seeded and aided by the addition of occasional small portions of water as minute, glistening rhombs. The base melts constantly at 110–111° with slight preliminary softening and gives $[\alpha]_D^{29}$ + 87.1° in absolute alcohol; $c = 0.804$. In its properties it resembles the methyl homolog, but is even more easily soluble.

Analyses. Calc. for $C_{23}H_{34}O_2N_2$: C, 74.54; H, 9.25; N, 7.57. Found: C, 74.87; H, 9.46; N, 7.68.

Summary

Cinchona alkaloids of the cinchonicine and quinicine type, reduced with palladium and hydrogen, yield mixtures of stereoisomers of a new type of alkaloids which we have called dihydrochonicinols and dihydroquinicinols. In general the *d*- forms proved easier to isolate. A number of the *d*- bases, one of the *l*- bases, and numerous salts of the *d*- and *l*- forms are described.

NEW YORK, N. Y.

THE AUTOXIDATION OF ETHYL ETHER

BY A. M. CLOVER

When a glass-stoppered bottle of ordinary ethyl ether is allowed to stand for several months, it is known to acquire oxidizing properties which are usually attributed to hydrogen peroxide or to "ethyl peroxide." When this impure ether is allowed to evaporate in an open vessel, a liquid residue remains which possesses, besides these oxidizing properties, a very pungent odor. The residue completely disappears in time, through evaporation.

Frequent references occur in pharmaceutical literature to explosions[1]

[1] Schär, *Arch. Pharm.*, **225**, 623 (1887). Cleve, *Chem. News*, **63**, 101 (1891); *Pharm. Ztg.*, **34**, 426 (1889). Neander. *Chem. Ztg.*, **26**, 336 (1902).

which have resulted from ether residues. Other impurities including acetic aldehyde and acid are known to be formed in ether on standing and all of these impurities are of importance in connection with the use of ether as a solvent and especially as an anesthetic in medicine. The action of air upon ether appears to be of particular interest because we have here a case of peroxide formation by autoxidation of a very stable substance, whereas from chemical experience we are led to expect such behavior only with unsaturated or highly reducing substances.

Schonbein[2] first noted the formation of an oxidizing substance in ether and this has since been referred to frequently as hydrogen peroxide.[3] Berthelot[4] considered the peroxide of ether to be identical with "ethyl peroxide" which he had obtained by the action of ozone upon ether. Nef[5] assumed that oxidized ether contained diacetyl peroxide.

The Accumulation of Active Oxygen in Ether

Dunstan and Dymond[6] and also E. v. Neander[7] determined the active oxygen content of certain samples of ether by means of their action upon an acidified solution of potassium iodide. This method has been found to be reliable for quantitative work. A few cubic centimeters of the ether is dissolved in a dilute solution of potassium iodide, acidified with sulfuric acid and the solution is then allowed to stand for 15 minutes. The free iodine is determined with sodium thiosulfate. For very accurate work a control experiment may be used.

Several years ago Mr. R. L. Perkins and the writer first studied the gradual development of ether peroxide[8] by frequently charging cork-stoppered bottles of ether with air. At the end of 5 or 6 weeks the active oxygen content of the solutions reached a maximum which was only about $0.01 \ N$. Later, it was discovered that when an ordinary glass-stoppered reagent bottle was partly filled with ether and allowed to stand in a light place there was not only a continuous development of peroxide, but the development took place at a gradually increasing rate.

All ether used in this work was carefully purified by shaking it several times with $1/3$ volume of water, then allowing it to stand for about a month over 20% sodium hydroxide in amber glass bottles; finally it was distilled. It was desired to remove especially all traces of alcohol

² Schönbein, *J. Chem. Soc.*, **4**, 134 (1852); *J. prakt. Chem.*, [1] **52**, 135 (1851).

³ Buchner, *Chem. Ztg.*, **9**, 691 (1885). Richardson and Fortey, *J. Chem. Soc.*, **69**, 1352 (1896). Kingzett, "Year Book of Pharm." **1876**, p. 554; *Chem. News*, **34**, 135 (1876).

⁴ Berthelot, *Compt. rend.*, **108**, 543 (1889); **92**, 895 (1881).

⁵ Nef, *Ann.*, **298**, 202 (1897).

⁶ Dunstan and Dymond, *J. Chem. Soc.*, **57**, 574 (1890).

⁷ Neander, Ref. 1.

⁸ This term will be applied to the organic peroxide which, as will be shown, is derived directly by the action of oxygen upon ether.

and aldehyde as these are later formed by decomposition of ether peroxide. The ether was not especially dried. No better method of oxidation could be discovered than the one already described. Glass-stoppered bottles $2/3$ filled were allowed to stand in a light place without further attention. The reaction is very slow at first and at least 6 weeks is required for the solution to become $0.01\ N$ in active oxygen. As the accumulation of peroxide proceeds, the rate of peroxidation increases greatly and during the summer season, providing the heat is not excessive, several per cent. of peroxide is developed at the end of 5 or 6 months. The strength of these solutions is due partly to loss of ether by evaporation.

Light has a very important influence upon the peroxidation, but it does not appear to be indispensable. A bottle of purified ether in amber glass was well protected from light and at the end of 6 months no peroxide could be detected. On the other hand, a sample which had not been especially purified, but was free from peroxide, did develop a small amount of the latter under the same conditions. Also, it is a fact that ether sealed in tin cans for use in anesthesia frequently develops peroxide although free from the latter originally. That light is not essential to peroxidation is proved by the following experiment. A glass-stoppered amber bottle was partly filled with ether in which peroxide had been accumulating for some time and the bottle was well protected from light. At the beginning, the solution was $0.125\ N$ in active oxygen. At the end of 12 weeks, the ether had evaporated to just about $1/2$ the original volume but the concentration of peroxide had increased 4-fold to $0.525\ N$. It seems that light is much more important in starting the peroxidation than it is at a later stage, and it has been found that bottles of ether which had started to oxidize during the winter season of short daylight progressed much more slowly than those started in the summer season.

Direct sunlight was found to have a favorable influence upon the accumulation of peroxide up to a certain point, and with further exposure there was a decrease. It will be shown later that ether peroxide is broken down by light and it is probably because of the pronounced decomposition by direct sunlight that it was found impossible to obtain solutions of any considerable strength in this way.

Catalytic Action of Acetaldehyde.—An explanation was desired of the progressive increase in the rate of peroxidation and attention was directed to the influence of decomposition products of the peroxide. It was discovered that with samples of ether which had reached a fairly rapid rate of peroxidation, the latter came to a standstill if a portion of the ether were volatilized, and the conclusion was drawn that the influence was due to a volatile product. Experiments showed that carbon dioxide, carbon monoxide, ethylene and alcohol were without effect. Acetaldehyde, which is known to be one of the products of spontaneous decomposition,

was also tried. When this substance was added to pure ether, one part in 1000, the amount of peroxide found at the end of 2 months was about twice that which had developed in the pure ether. When 0.5% of aldehyde was added the effect was decidedly greater, and it appears from the experiments performed that such an amount would be necessary to explain the rapid accumulation of peroxide in ether after long standing.

Development of Hydrogen Peroxide.—Inasmuch as the peroxide contained in ether has been so frequently referred to as hydrogen peroxide, it is of first importance to determine whether the latter substance is a primary product of oxidation, as has been frequently assumed, or whether it is the result of a secondary reaction. It is also important to determine to what extent hydrogen peroxide is present along with ether peroxide and to be able to separate the two.

The **Chromic Acid Test.**—This method of detecting traces of hydrogen peroxide in ether is capable of great delicacy if care be taken to use only a limited amount of sulfuric acid. Hydrogen peroxide to the extent of 0.001% may be detected. Ether peroxide does not respond to this test.

A great many samples of ether have been tested from time to time during the course of oxidation and in no case has it been possible to obtain a positive test for hydrogen peroxide before the end of 3 or 4 months. Usually, at this time there has accumulated in the solution from 0.25 to 0.5% of ether peroxide. The amount of hydrogen peroxide increases slowly with time, but it has never been found to be more than a few per cent. of the amount of ether peroxide. Later it will be shown that ether peroxide reacts slowly with water to form hydrogen peroxide and this reaction, which may be assumed to take place to a very limited extent in ether solution, will account for the hydrogen peroxide. It appears certain that *hydrogen peroxide is not a primary product of oxidation.*

A confirmation of the conclusion drawn from the chromic acid test may be obtained by shaking out oxidized ether with water. Hydrogen peroxide may be completely removed in this way because it is a great deal more soluble in water than it is in ether. The ether peroxide, on the other hand, is more soluble in ether than in water and by repeated extractions an approximate separation of the two may be effected.

Ether Peroxide

Along with hydrogen peroxide, there is developed in the oxidized ether a relatively small amount of acetic acid.[9] Alcohol in considerable quantity and also aldehyde are formed as secondary products, as will be shown later. Also, it is likely that derivatives of the above substances are present. These secondary or decomposition products of ether peroxide may be easily removed and the primary product of peroxidation may be obtained in a practically pure state as follows.

9 Richardson and Fortey, Ref. 3.

A sample of oxidized ether which had stood about 6 months was about 0.35 N in active oxygen. It was shaken out twice with $1/4$ volume of water and then gave no test for hydrogen peroxide with chromic acid. The ether was dried by means of anhydrous sodium sulfate. Portions of a few cubic centimeters each of the solution were removed to small weighed flasks and the weights of residues obtained after they had been allowed to remain in a continuous vacuum for different periods of time. In each case a determination of the active oxygen content of the residue was made in the usual manner using a solution of potassium iodide acidified with sulfuric acid. The ether solution was about 0.3 N in active oxygen and approximately 4 cc. was removed for each experiment.

Expt.	In vacuum Min.	Wt. of residue G.	0.1 N Thio- sulfate Cc.	Active oxygen %
I	15	0.0638	10.6	13.29
II	25	0.0526	9.65	14.67
III	55	0.0456	8.45	14.82
IV	100	0.0336	6.25	14.88
V	300	0.0003	.00	..

Calculated active O for $C_4H_{10}O_3 = 15.09$

In Expt. V the vacuum was maintained for half a day until all odor was gone. No more peroxide was found to be present although apparently a trace of non-volatile matter remained.

The above experiments were carried out in the summer of 1920. A year later an attempt was made to duplicate them with a sample of ether which had stood for 4 or 5 months. During the later 2 months the temperature was unusually high and peroxide had not accumulated as rapidly as had been expected; also it was found to be contaminated with a few per cent. of non-volatile matter. In one sample the active oxygen was found to be 13.75%. After correcting for non-volatile matter it was 14.3%.

Recently, the oxidation of a sample of pure ether has been hastened by the addition of about 0.5% of aldehyde. At the end of 6 weeks, the solution was 0.15 N in active oxygen. Acetic acid was present to the extent of about 0.1%. There was no evidence of the presence of peracid. The ether solution was shaken well with $1/3$ of its volume of dil. sodium hydrogen carbonate solution and was then allowed to evaporate to about $1/3$ volume. After the solution had been thoroughly dried over sodium sulfate the residue was analyzed as usual. A residue of 0.0422 g. obtained after the sample had remained in a vacuum for 1 hour required 7.3 cc. of 0.1 N thiosulfate solution. The non-volatile residue obtained from an equal amount of the ether solution was 0.0028 g. After correcting for the residue the active oxygen was found to be 14.82%.

Ether peroxide is miscible with water, alcohol, ether and acetone and

has a limited solubility in benzol, chloroform and petroleum ether. The boiling point is unknown, as no attempt was made to distil it on account of the great danger involved. It is somewhat volatile. When the solvent is mostly removed from a solution in ether nearly 10% of the peroxide also passes off. This decided volatility shows that it has the simple formula, only 1 molecule of ether or 2 ethyl groups being involved. It has a very irritating taste and odor and is also very irritating to the skin. It yields iodoform with alkali and potassium iodide. When the peroxide is dissolved in an excess of sodium hydroxide the active oxygen gradually disappears from the solution and, at the end of an hour, it has become dark yellow in color. On heating this solution and then acidifying it, a resinous substance is precipitated. When the acidified product is subjected to distillation, the presence of alcohol is shown by the iodoform test.

The following tests were made with a 6% water solution of the peroxide which was free from hydrogen peroxide and ether. The action on platinum black is very feeble when compared to that of hydrogen peroxide. Neither ferric chloride nor manganous chloride shows any catalytic effect upon the active oxygen, but with manganese dioxide and silver oxide oxygen is freely evolved. There appears to be no effect produced by either mercury or finely divided silver. Unlike hydrogen peroxide, it colors both guaiacum and benzidine directly. No precipitate is produced by barium hydroxide and as has already been pointed out, it gives no coloration with chromic acid. In the latter case, care must be used in restricting the amount of sulfuric acid or sufficient hydrogen peroxide will be formed by hydrolysis to respond to the test.

The *ratio of distribution* of ether peroxide between water and ether has already been stated to be very different from that of hydrogen peroxide. Walton and Lewis[10] determined this ratio for hydrogen peroxide at 25° and found the coefficient to be 9.11 when the water contained about 5% peroxide and 8.25 with a solution which was nearly 10% peroxide. The writer has tried more dilute solutions at about the same temperature. With aqueous solutions of 1% and 2.8% of hydrogen peroxide, a coefficient of approximately 16 was obtained in each case. The peroxide was determined through its action on potassium iodide in acid solution. Equal volumes of the two solvents were used. The coefficient for ether peroxide has been found to vary between 1.70 and 2.0 in different experiments, the peroxide being more soluble in ether than in water. Ether solutions of peroxide varying in strength from 0.05% to 0.5% were used.

The *acidic nature* of ether peroxide is worthy of note. This is shown by the fact that the ratio of distribution between ether and water is greatly changed by the presence of alkali, much more of the peroxide being present in the alkaline solution.

    [10] Walton and Lewis, THIS JOURNAL, **38**, 633 (1916).

Spontaneous Decomposition of Ether Peroxide

Attention has already been directed to the formation of a small amount of hydrogen peroxide which is probably the result of a hydrolytic reaction. Ether peroxide, like other organic peroxides, might be expected to be unstable and especially in solution and under the influence of light to break down into simpler substances. This is found to be a fact. The percentage decomposition of a dilute solution is much greater than that of a strong solution. When protected from light the peroxide also decomposes but more slowly than upon exposure.

A solution (about 0.3 N) was exposed to the action of diffused light in a flint-glass bottle with a cork stopper inserted as tightly as possible. After standing for 2 weeks during the month of December, the stopper was removed and there was a continuous evolution of gas lasting several minutes. The solution had lost $1/3$ of its strength. A fresh stopper was inserted and the decomposition allowed to continue for 4 weeks longer when the strength was found to be less than $1/2$ of the original. Six weeks later, all but 10% of the original peroxide had disappeared and gaseous products continued to be formed.

Another experiment of a similar kind was carried out. Before the removal of the stopper the bottle was cooled in ice water and a stopper containing a capillary tube was inserted so that the gas which escaped as the bottle again came to room temperature could be collected. The presence of a determinable quantity of carbon dioxide was shown by passing the gas through baryta water. By means of water the gas was washed practically free from ether. There was no further decrease in volume on standing over bromine water or a solution of cuprous chloride. The residual gas after removal of carbon dioxide and ether burned with a blue flame and was undoubtedly methane.

The ether solution in which less than 10% of the original peroxide now remained was subjected to a slow distillation from a flask which was immersed in a vessel of warm water. The distillate was redistilled to remove all peroxide as the latter is somewhat volatile. The product now gave a heavy iodoform test and also responded readily to the test for aldehyde with ammoniacal silver nitrate. When shaken with a 10% solution of potassium hydroxide a yellow color appeared in a few minutes.

The experiment was repeated with a solution 0.45 N in active oxygen. The bottle stood from February 11 to April 19 and the stopper was removed several times to relieve the pressure. The gas was tested with the same results as before. On April 19 the amount of peroxide was only 3% of the original. About 100 cc. of the ether was slowly distilled as before. The first portion of the distillate was tested for aldehyde with the same result as before. The second portion, which was about $1/2$ of the total, was dried over potassium carbonate, then treated with 1.5 g. of p-nitrobenzoyl chloride. After 2 days the ether was evaporated. From the residue after treatment with sodium carbonate solution, there was obtained more than 0.5 g. of the ethyl ester of the above acid; m. p. 56° (crystallized from petroleum ether).

Berthelot[11] demonstrated the formation of *methane* by the action of air upon ether which had been exposed to direct sunlight for several weeks. Berthelot first calls attention to the fact that alcohol is also one of the products formed. The methane was obtained mixed with the residual nitrogen of the air and as the author does not state the experimental

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[11] Berthelot, *Compt. rend.*, **129**, 627 (1899).

basis for his conclusion that methane is formed, it must be assumed that an analysis of the gas was made. No carbon dioxide was found.

The *development of acetic acid* in ether has been found to be very much slower than that of peroxide. Even after several months', oxidation the amount of acid, as determined by titration, is not over a few per cent. of the amount of peroxide in the solution. After long standing of an ether bottle during which time a large part of the ether had evaporated, the acid content has been found to be as high as 1%. It does not seem likely that the acid is a direct product of decomposition of the peroxide, and its presence may be accounted for by autoxidation of aldehyde. Experiment has shown that during the decomposition of peroxide in tightly stoppered bottles the increase in acidity was relatively very small in proportion to the amount of peroxide decomposed, and this change likewise could be accounted for by autoxidation of aldehyde.

Action of Dilute Acid on Ether Peroxide

When the peroxide is dissolved in water and the solution allowed to stand, hydrogen peroxide is slowly formed, as shown by the chromic acid test. After several weeks the greater part of the active oxygen is present as hydrogen peroxide, this fact being shown by the ratio of distribution of the active oxygen when the water solution is shaken with pure ether. The formation of hydrogen peroxide is greatly facilitated by the presence of mineral acid and, in fact, the complete conversion of the active oxygen may be brought about by this means in a short time.

Four hundred and fifty cc. of oxidized ether, which was about normal in active oxygen and, accordingly, a little more than 5% in ether peroxide, was shaken out with 50 cc. water and the water extract preserved. The ether was distilled in a vacuum nearly to completion. One hundred cc. of water was then added and this solution was freed from ether *in vacuo*. The distillation in a vacuum was continued by immersing the distilling flask in a vessel of water at 50°. About 15 cc. was distilled, which presumably contained most of the remaining alcohol. The solution in the flask now contained about 90% of the active oxygen present at the beginning, or about 22.5 g. of ether peroxide. A few drops of dil. sulfuric acid were added and the solution was allowed to stand at 60° for 2 or 3 hours after which it was subjected to distillation at ordinary pressure. A strong odor of acetaldehyde was noted. About $1/2$ of the liquid was distilled and the distillate was treated with potassium carbonate, whereupon about 15 cc. separated to the top. The liquid was dried further with fresh anhydrous potassium carbonate and became colored on standing. On distillation it did not show a constant boiling point although most of it passed over below 80°. The product is mostly alcohol contaminated with derivatives of acetaldehyde. Probably paraldehyde and the mono-acetal, $CH_3CH(OH)(OC_2H_5)$, are present.

After distilling the product of hydrolysis of the peroxide, there remained a solution of hydrogen peroxide which was found to be of nearly 12% strength. A portion of it was converted directly into succinic acid peroxide as follows. Ten cc. of the solution was diluted with 5 cc. of water and 5 g. of small crystals of succinic anhydride added. The mixture was shaken frequently during the course of 45 minutes. After filtering, washing and drying, about 1.5 g. of pure succinic acid peroxide was obtained.

Analysis.   Calc. for $C_8H_{10}O_8$: O (active), 6.84.   Found: 6.76.

The water extract of the original peroxide solution was then diluted with an equal volume of water and this subjected to distillation at reduced pressure, the temperature of the heating bath being about 60° to 65°.   Approximately $1/4$ of the total was distilled. This distillate was found to contain only a negligible amount of peroxide and was partly redistilled.   This last distillate gave a decided iodoform reaction, but no tests for aldehyde.   When it was treated with solid potassium carbonate, about 1 cc. of alcohol separated.   The latter was dissolved in 15 cc. of alcohol-free ether which had been dried over anhydrous potassium carbonate.   About 3 g. of *p*-nitrobenzoyl chloride was added and, after standing several days, nearly 3 g. of the ethyl ester was obtained; m. p. after recrystallization from alcohol, 55–56°.

In another experiment the hydrolysis of the peroxide was allowed to proceed in acid solution at 45° and no change was noted in the general result.   In this case it was ascertained that during the hydrolysis there was little, if any, loss in active oxygen. A small volume of the solution at the beginning and at the end of the experiment gave practically the same values.   The formation of a considerable amount of aldehyde or its derivatives was shown by the formation of resinous matter on treating the distillates with caustic alkali.

Acetic Peroxide and the Theory of Nef.—If acetic peroxide were present in oxidized ether its identification would be relatively simple as it soon changes to acetic peracid when dissolved in water, and the latter substance is characterized by the rapidity of its action upon potassium iodide.   Iodine is precipitated at once from a very dilute solution of the former.[12]   At no time has it been possible to detect this substance.   Again, the theory of Nef assumes that hydrogen peroxide is formed as a direct product of oxidation and there is no experimental evidence for such an assumption.

"Ethyl Peroxide."—Without doubt the idea of Berthelot concerning the structure of this substance was that 2 molecules of ether take on an extra atom of oxygen just as barium oxide does at a high temperature, and that in the formation of "ethyl peroxide," $(C_2H_5)_4O_3$, no change takes place in the ethyl groups.   Since the time of Berthelot's publication Baeyer and Villiger[13] have synthesized diethyl peroxide, $(C_2H_5)_2O_2$, an ether-like body which, unlike Berthelot's product, is very difficult to reduce and does not react with water to form hydrogen peroxide.   Harries[14] also studied the action of ozone on dry ether at low temperature and subjected the product to distillation in a vacuum.   A peroxide-containing distillate was obtained, but the results of elementary analyses were not concordant nor were they close to those required for Berthelot's formula. We may conclude from the literature that "ethyl peroxide" possibly consists, at least partly, of ether peroxide, but this is not strictly proved. There does not appear to be much of an experimental basis for the formula of Berthelot.

[12] Baeyer and Villiger, *Ber.*, **33**, 1575 (1900).

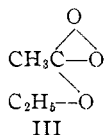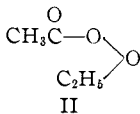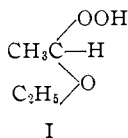[13] Baeyer and Villiger, *ibid.*, **33**, 3337 (1900).

[14] Harries, *Ann.*, **343**, 375 (1905).

The Structure of Ether Peroxide

The following facts are to be considered. (A) The active oxygen content of the pure peroxide is approximately that required for a substance formed by the addition of one molecule of oxygen to one molecule of ether, $1/2$ of the added oxygen being active. (B) The peroxide is formed directly by the action of oxygen upon ether. (C) It is volatile. (D) It decomposes, especially under the influence of light, with the formation of carbon dioxide, methane, aldehyde and alcohol. (E) It reacts with acidified water to yield hydrogen peroxide quantitatively. Alcohol and aldehyde are also formed in considerable quantity. (F) Ether peroxide is acidic.

That the ethyl group is directly attacked in the peroxidation is proved by (E), since aldehyde could not be formed here as the result of a secondary oxidation, except at the expense of active oxygen. That only one ethyl group enters into reaction with oxygen is shown by both (D) and (E) because in both cases considerable quantities of alcohol are formed. That the hydrogen of only one carbon atom has been affected is shown by the formation of methane (D). The acidic nature of the peroxide indicates the presence of an OOH group, for both the mono-alkyl and mono-acyl derivatives of hydrogen peroxide are known to form salts.

If hydrogen *is not removed*, but merely displaced, we have the following structure (I) which is α-ethoxyethyl hydrogen peroxide.

$$
\underset{\text{I}}{\begin{matrix} \text{CH}_3\text{C} \diagup\!\!{}^{\text{OOH}}_{\text{—H}} \\ \text{C}_2\text{H}_5 \!\!\diagup\!\!{}^{\text{O}} \end{matrix}}
\qquad
\underset{\text{II}}{\begin{matrix} \text{CH}_3\text{C}\overset{\text{O}}{}\text{—O} \\ \text{C}_2\text{H}_5 \end{matrix}\!\!\diagdown\!\!{}_{\text{O}}}
\qquad
\underset{\text{III}}{\begin{matrix} \text{CH}_3\text{C}\overset{\text{O}}{\triangle}\text{—O} \\ \text{C}_2\text{H}_5\text{--O} \end{matrix}}
$$

If hydrogen *is removed*, ethyl peracetate (II) might be formed which differs from (I) by having 2 atoms less of hydrogen.

Baeyer and Villiger[15] state that the odor of the latter substance is similar to chloride of lime. This cannot be said of ether peroxide. Also according to Baeyer and Villiger, ethyl peracetate yields ethyl hydrogen peroxide upon treatment with alkali, and the latter has been shown by the same authors to be stable in alkaline solution. Ether peroxide, on the other hand, when treated with alkali soon loses its active oxygen and is converted into a resinous product. Such a very improbable structure as (III) which would be isomeric with ethyl peracetate could not yield aldehyde on hydrolysis except by loss of active oxygen. Also, it would be difficult to explain the formation of methane and alcohol by the decomposing action of light.

Formula I is in agreement with all the experimental facts and therefore represents the true structure of ether peroxide. Accordingly the latter is formed simply by the displacement of one hydrogen atom of a methylene

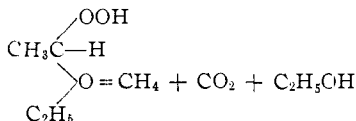[15] Baeyer and Villiger, *Ber.*, **34**, 746 (1901).

group by one molecule of oxygen, the net result being the addition
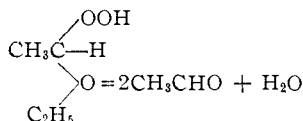of a molecule of oxygen to a molecule of ether. $\begin{array}{c}CH_3CH_2\\ \diagdown \\ \diagup \\ C_2H_5\end{array}O + O_2 =$
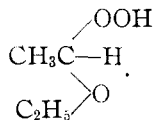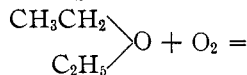
$\begin{array}{c}\diagup OOH\\ CH_3C{-}H\\ \diagdown \diagup O\\ C_2H_5\end{array}$. This conclusion is strengthened by the highly probable

theory of Baeyer and Villiger[16] concerning the autoxidation of benzalde-
hyde which takes place as follows: $C_6H_5C\overset{\diagup H}{=}O + O_2 = C_6H_5C\overset{\diagup OOH}{=}O$.

Under the influence of light the decomposition of ether peroxide takes
place in two ways.

$\begin{array}{c}\diagup OOH\\ CH_3C{-}H\\ \diagdown O\\ \diagup\\ C_2H_5\end{array}O = CH_4 + CO_2 + C_2H_5OH$ $\begin{array}{c}\diagup OOH\\ CH_3C{-}H\\ \diagdown O\\ \diagup\\ C_2H_5\end{array}O = 2CH_3CHO + H_2O$

(1)   (2)

The action of acidulated water is as follows: $\begin{array}{c}\diagup OOH\\ CH_3CH\\ \diagdown O\\ \diagup\\ C_2H_5\end{array}O + H_2O =$
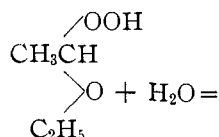
$CH_3CHO + C_2H_5OH + H_2O_2$. It is possible that to some extent the

mono-acetal is formed $\begin{array}{c}\diagup OOH\\ CH_3CH\\ \diagdown O\\ \diagup\\ C_2H_5\end{array}O + H_2O = \begin{array}{c}\diagup OH\\ CH_3CH\\ \diagdown O\\ \diagup\\ C_2H_5\end{array}O + H_2O_2.$

The results obtained with ethyl ether have naturally suggested a study
of other ethers and a number of these have been tried in a preliminary way.
All have been found to undergo peroxidation. The rapidity of peroxide
formation appears to increase with increasing size of the molecule although
a pronounced progressive increase in the rate like that with ethyl ether
has not been observed with butyl or amyl ethers. Ethers containing
a benzyl group oxidize more rapidly than those of the aliphatic group
and in the case of benzyl methyl ether, peroxidation takes place to the ex-
tent of 20–25% in the course of a month. A study of the peroxidation
of ethers is being continued.

Summary

Ether absorbs oxygen from the air, very slowly at first with the forma-
tion of a peroxide by direct addition. The rate of peroxidation becomes

[16] Ref. 12, p. 1569.

much greater in time due to the catalytic influence of acetic aldehyde, the latter being formed by spontaneous decomposition of the peroxide.

Ether peroxide has been prepared in sufficient quantity to permit a study of its properties and decomposition products, and a structural formula has been assigned to it.

DETROIT, MICHIGAN

PRELIMINARY STUDY ON THE FORMATION OF MALIC ACID

By JOHN MORRIS WEISS AND CHARLES R. DOWNS

Until comparatively recently very little maleic, fumaric and malic acids have been available to the chemist for investigation. The difficulty of obtaining even moderate quantities from natural sources discouraged work along these lines and a considerable portion of the data in the literature is inaccurate and misleading owing to the meagre quantities with which chemists had to deal. The authors[1,2] described a method for the synthesis of maleic acid by the partial oxidation of benzene in the presence of a catalyst which has resulted in ample supplies of material becoming available. We desire here to present some results on the reactions of maleic, fumaric and malic acids in respect to the transformation of maleic acid to fumaric acid and malic acid and of fumaric acid to malic acid.

The earliest work on the transformation of fumaric acid to malic acid was carried on by F. Loydl[3] who heated fumaric acid with dil. caustic soda solution at about 100° for 100 hours and in this way converted about 52% of the fumaric acid into malic acid. He states that the malic acid is deliquescent in a moist atmosphere, optically inactive and decomposes at 200° into water and fumaric acid without giving a trace of maleic acid.

E. Yungfleisch[4] claims that malic acid with a small amount of water is converted almost completely to fumaric acid when heated in a sealed tube at 180°. As the proportion of water is not stated, the results are of questionable value. He further states that at 150° in the presence of a large excess of water fumaric acid is converted in part to malic acid which latter is identical with inactive malic acid.

A. Pictet[5] repeated the latter part of Yungfleisch's work on the preparation of malic acid. He gives no experimental details of the reaction but describes the product as non-deliquescent and decomposing at 135°, giving maleic anhydride and water in the distillate and fumaric acid in the residue. He decided that he obtained a different product from that of Loydl,[3] not realizing that the latter probably obtained an impure product by the method he employed, and concluded that there were probably two varieties of inactive malic acid corresponding to racemic and meso-tartaric acids.

[1] Weiss and Downs, *J. Ind. Eng. Chem.*, **12**, 228 (1920).

[2] U. S. pats. 1,318,631; 1,318,632; 1,318,633; 1,377,534.

[3] Loydl, *Ann.*, **192**, 80 (1878).

[4] Yungfleisch, *Bull. soc. chim.*, **30**, 147 (1878).

[5] Pictet, *Ber.*, **14**, 2648 (1881).