the $\alpha,\beta$ or $\alpha,\gamma$ derivatives in his mixtures, it is possible that refined methods may show that they also are produced, although probably in small quantities. The toxicity of these compounds is being investigated by Dr. Charles H. Richardson of the Bureau of Entomology, who will later report on his findings.

## Summary

1. The preparation and separation of $\alpha,\alpha$, $\beta,\beta$, $\beta,\gamma$, and $\gamma,\gamma$ dipyridyls produced by a new method involving the interaction of sodium, pyridine and dry oxygen or air is described.

2. $\beta,\gamma$-Dipyridyl has been isolated and some of its properties are given. This represents the only dipyridyl of the six possible isomers previously not reported.

3. The proportions of the various dipyridyls produced depend principally on the time, temperature and pressure of the preliminary digestion of the sodium dipyridine in an excess of pyridine before the oxidation is begun. These variations are being further studied.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT OF PARKE, DAVIS AND COMPANY]

# AUTO-OXIDATION OF ETHERS

BY A. M. CLOVER

RECEIVED AUGUST 18, 1923

In a previous article[1] on the auto-oxidation of ethyl ether, the writer has called attention to the fact that other ethers, when exposed to the action of the air, take on oxidizing properties, which may be shown by shaking them with an acidified solution of potassium iodide. As most ethers are insoluble it is necessary in order to obtain a complete reaction to add an equal volume of acetic acid to the solution of potassium iodide which contains an equivalent amount of hydrochloric acid. About 15 cc. of this solution is freshly prepared and half of this used as a control. One-half to 1 cc. of the ether to be tested is shaken with the solution for about a minute, then diluted with 20 volumes of water and the iodine determined by titration with thiosulfate solution. The results obtained in this way have been concordant.

As the peroxide is the primary product of oxidation, its determination from time to time is helpful in a study of this nature. However, the amount of peroxide found at any given time does not correspond to an equivalent amount of the ether because more or less of the total peroxide will have spontaneously decomposed. The peroxide usually accumulates until it reaches a definite maximum value. Further examination of such

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[1] Clover, THIS JOURNAL, **44**, 1107 (1922).

a solution has been found to be very difficult because of the general instability of the peroxides. No general method of procedure has been followed.

Exposure for oxidation has been made in both diffused light and sunlight. A glass-stoppered bottle was usually about $^1/_3$ filled and a piece of tin foil was placed in the neck to prevent the accumulation of a film of ether. Bottles which were exposed to sunlight were placed in such a position that they might receive direct rays of the sun during the entire day. The stopper and neck of each bottle were covered by an inverted beaker to prevent the access of rain drops.

## Propyl Ether

The substance was prepared by the action of sulfuric acid upon *n*-propyl alcohol; b. p., 84–91°. After 9 months the ether had become about 0.5 *N* in active oxygen. The amount of free acid was relatively small, being 0.015 *N*.

About 10% of the active oxygen represented hydrogen peroxide which was removed by shaking the product twice with an equal volume of water. The ether peroxide does not give the chromic acid test. It was purified in small portions in the same manner previously employed in purifying ethyl ether peroxide. For analysis, the residues were evaporated in a vacuum until nearly $^1/_3$ of the peroxide had volatilized. In time the peroxide was completely removed leaving only a trace of inactive matter.

*Analyses.* Subs., 0.0583, 0.0623: 8.8 cc., 9.05 cc. of 0.1 *N* thiosulfate. Calc. for $(C_3H_7)_2O.O_2$: active O, 11.94. Found: 12.1, 11.6.

The propyl ether peroxide has a pungent odor and is moderately soluble in water. When the solution is warmed with a little mineral acid it is hydrolyzed into hydrogen peroxide and a decided odor of an aldehyde is noted.

**Oxidation in Sunlight.**—In general, the result was decidedly different from that obtained in diffused light. The development of peroxide was slow and at the end of nearly six months the product was only 0.075 *N*. On the other hand, the ether had been partly changed into ester and free acid, the latter being 0.55 *N*. No appreciable amount of hydrogen peroxide was present at any time. The product was finally transferred to a cork-stoppered bottle which was nearly filled; the exposure was continued in order to bring about complete decomposition of the peroxide.

The decomposition product was extracted with an excess of water containing sufficient sodium bicarbonate to remove all free acid. The extract was subjected to distillation and the distillate was redistilled. The first fraction contained a small amount of dipropyl ether. It also possessed the odor of an *aldehyde*, reduced ammoniacal silver nitrate and was oxidized to acid on standing in the air. The second fraction was treated with dry potassium carbonate and the *alcohol* which separated was again dried and then distilled. It boiled at about 80–95° and was miscible with water. It was converted into the benzoate which distilled at about 226.5° (corr.) which is 4° lower than the boiling point of propyl benzoate.

The aqueous residue containing sodium salt was acidified with an excess of sulfuric acid and distilled until all volatile acid had been removed. The distillate was free from hydrochloric and sulfuric acids. A portion which required 35.2 cc. of 0.1 *N* sodium hydroxide gave 0.291 g. of sodium salt after drying at 160°. The equivalent weight of this salt is calculated to be 82.6 which is much too low for that of sodium propionate (96).

The extracted ether was saponified and the equivalent weight of sodium salt was found to be 81.1. Calculation also showed that the amount of ester was equivalent to about 5% dipropyl ether per volume.

### Isopropyl Ether

After a sample of this substance[2] had been shaken well with water and dried over calcium chloride, it distilled at 68–70° and was free from peroxides. On standing from April to October, the solution gradually acquired active oxygen at a regular rate and became about *N* in this substance. A good portion was in the form of hydrogen peroxide and practically all of this was removed on shaking the ether twice with an equal volume of water. Analyses of residues obtained by evaporating the product in a vacuum showed that the new peroxide is not a simple ether peroxide, $R_2O.O_2$, for the percentage of active oxygen was found to be far too high. The peroxide residue had an irritating odor, was soluble in water and did not give the chromic acid test. It was volatile except for a very small part, which also appeared to be of a peroxide nature.

**Hydrolysis.**—The peroxide residue is converted into hydrogen peroxide by hydrolysis and the change is quantitative. *Acetone* is also formed. The reaction is brought about in dilute acid solution during 24 hours. At the end of this time no unchanged peroxide may be extracted with ether. The hydrolyzed product was subjected to distillation and acetone identified by conversion into dibenzalacetone; m. p., 112°.

***iso*Propyl Alcohol a Product of Decomposition.**—A portion of the ether which had oxidized for 6 months was shaken twice with an equal volume of water. Dil. sulfuric acid was then added to the extract and it was allowed to stand for a few days for complete hydrolysis of the peroxide. The product was then partly distilled and the same process repeated with the distillate. A water solution was obtained from which an insoluble layer was separated by means of potassium carbonate. After having been dried this substance boiled at 62–67°. It contained some acetone which resulted from hydrolysis of the peroxide. It reacted readily with *p*-nitro-

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[2] Secured from the Standard Oil Company of New Jersey.

benzoyl chloride and yielded a good quantity of the *iso*propyl ester; m. p., 108–9°, after recrystallization from petroleum ether. *iso*Propyl alcohol is formed during the early stages of auto-oxidation and is not an hydrolysis product of the peroxide. This was proved by an experiment similar to the above in which a peroxide residue was used after it had remained in a vacuum for some time. From the hydrolyzed solution it was found impossible to obtain any of the *iso*propyl ester described above.

**Nature of the Peroxide.**—The simple ether peroxide, $(C_3H_7)_2O.O_2$, should contain 11.9% of active oxygen, but the values actually obtained from residues, free from hydrogen peroxide, varied from 15% to 26%. As *iso*propyl alcohol was found to be a product of the auto-oxidation, it was suspected that the peroxide consisted partly of a simple derivative of acetone, the ether molecule having been broken.

Similar products have been prepared directly by the action of acetone upon hydrogen peroxide both in water and ether solution. These are readily soluble in water and are almost completely volatile. They possess an odor very similar to that of the *iso*propyl ether residue and in dilute aqueous solution are decomposed into their original constituents. They could not be brought to crystallization. The percentage of active oxygen varied from 25.1 to 26.5. The crystalline acetone peroxide of Wolffenstein[3] was not present. This is formed under certain conditions by the interaction of the two substances. In the present experiments a 2.5% solution of hydrogen peroxide in ether was allowed to stand for three days after being mixed with one molecular proportion of acetone. Also a 10% aqueous solution of pure hydrogen peroxide containing a little mineral acid was treated with half its volume of acetone and the mixture allowed to stand for three days. An interesting fact is the high percentage of active oxygen contained by the new product, the figures being considerably higher than that of the Wolffenstein substance or of any substance which could be formed by the interaction of acetone and hydrogen peroxide in molecular proportions.

## Normal Butyl Ether

The ether distilled at 140–142° at ordinary pressure. A partly filled bottle of it was allowed to oxidize in diffused light for a year, and became about *N* in active oxygen. When extracted with water the latter gave no test for hydrogen peroxide by means of chromic acid. A small amount of free acid had developed, the product being less than 0.1 *N*.

Small portions of the oxidized ether were placed in a small distilling flask which was immersed in a vessel of water at 65°. After a vacuum had been maintained for 1 to 1.5 hours, the unchanged ether together with 25 to 35% of the peroxide had been removed.

[3] Wolffenstein, *Ber.*, **28**, 2267 (1895).

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|---|---|---|---|
| Residue | 0.1260 | 0.0735 | 0.1388 |
| 0.1 *N* thiosulfate | 15.45 | 9.20 | 16.6 |
| Active oxygen, % | 9.81 | 10.01 | 9.57 |
| Calculated active oxygen, for $(C_4H_9)_2O.O_2$. | ... | ... | 9.87 |

**Butyl Ether Peroxide** is very sparingly soluble in water. The solubility in alkali is much greater so that most of the peroxide may be extracted from the ether by means of sodium hydroxide solution. However, some decomposition is brought about by this treatment. When the peroxide is warmed with dil. mineral acid, hydrogen peroxide is formed slowly. A 20% solution of the peroxide begins to evolve gas when heated to 110°. This process may be completed by heating the liquid for half an hour at 130°. The gas was found to consist of carbon dioxide and another portion which burned with a blue flame.

When the peroxide solution was stoppered tightly or sealed to prevent further action of the air, decomposition of the peroxide slowly took place. A little pressure was developed but the principal resulting substances were acid and ester. Butyric acid was present but it was not pure as the equivalent weight of the total volatile acid was lower than that of propionic.

**Oxidation at Higher Temperature.**—With increase in temperature the rate of development of peroxide also increases. The ether was exposed to the action of the air and the temperature maintained continuously at 70–75°. There was a gradual increase until at the end of nine days a maximum was reached and the product had become more than 1.5 *N* in active oxygen. Hydrogen peroxide and much free acid were present. The latter was removed by extraction with sodium bicarbonate and found to be nearly pure butyric acid. Butyl alcohol was present in the extract. The extracted product was then heated in an oil-bath at 130° until the evolution of gas had ceased, when it was distilled. It passed over completely at 125–155°. This distillate was found by saponification to contain considerable ester, presumably butyl butyrate.

**Oxidation in Sunlight.**—A sample was exposed for six months during the summer season. There was a gradual increase in peroxide to a concentration of about 0.4 *N*. Free acid amounted to about 0.7 *N*. Hydrogen peroxide was present, but the amount was relatively very small. A little water had separated from the solution. A portion of the product was then further exposed for decomposition of the peroxide as with propyl ether, about three weeks being required. The mixture was then extracted with an excess of water containing sufficient alkali to remove all free acid. Considerable butyl alcohol was distilled from the extract. After having been separated from the water and dried by means of solid potassium carbonate, it distilled at about 115°. The benzoate distilled at 236–239°. The extracted ether solution was distilled and nearly all passed over within a range of 35°, leaving only a little residue. The distillate was saponified with an excess of potassium hydroxide in alcohol. The potassium salt obtained was acidified with sulfuric acid and extracted with ether which was then dried by means of calcium chloride. The residue obtained on evaporation of the ether consisted mostly of butyric acid as the greater part of it distilled at 160–162°.

In another similar experiment the acid was extracted from the peroxide-free solution by means of alkali. A part of this extract was acidified with sulfuric acid and volatile acid completely removed by distillation. The equivalent weight of the sodium salt of this acid was found to be 103.4 when dried at 150° (sodium butyrate, 110). When the experiment was repeated and the acidified solution extracted twice with an equal volume of pure ether, nearly 90% of the total volatile acid was removed. The remainder was completely removed by distillation and the equivalent weight of the sodium salt found to be 76.3, which is considerably less than that of sodium acetate. It was therefore tested for *formic acid* with positive results. On treatment with concd. sulfuric acid a gas was evolved which burned with a blue flame. It also reduced mercuric acetate when it was heated with a solution of the latter in dil. acetic acid.

## Iso-Amyl Ether

The substance was redistilled before use; b. p., 168–171°. It accumulates active oxygen a little more rapidly than butyl ether, and a very small amount of hydrogen peroxide appears in time. In general, however, the results have merely confirmed those obtained with butyl ether. It was found impracticable to obtain a residue of pure peroxide on account of the high boiling point of the ether.

The peroxide slowly decomposed on standing when the oxidized ether was stoppered in a filled bottle. A solution which was largely decomposed was extracted with water containing sufficient sodium bicarbonate to remove the free acid. From the water solution a small amount of peroxide was removed by extraction with pure ether and the solution was then treated with sulfuric acid and distilled. Formic acid was identified by the usual tests and the presence of valerianic acid was shown by the limited solubility of the oily portion of the distillate.

**Action of Sunlight.**—A partly filled bottle was exposed for five and a half months through the summer period. It was 0.74 $N$ in active oxygen and 0.65 $N$ in acidity. A little water began to separate soon after exposure but at no time was there present in the ether an appreciable quantity of hydrogen peroxide. Complete decomposition was brought about by continued exposure of this product in the usual manner, but this required more time than with butyl ether. Free acid was removed by means of sodium carbonate. The solution of sodium salt was acidified with sulfuric acid and extracted with ether. The latter was dried with calcium chloride and the residue distilled after evaporation of the ether. It boiled from 163–173°. A small amount of viscous residue remained. Apparently the acid is largely *iso*valeric mixed with some *iso*butyric. A small amount of acid still lower in the series may be present. In another experiment the equivalent weight of the sodium salt of the combined volatile acid was found to be 111.3 and the presence of formic acid was proved.

The extracted oil distilled within a wide range. From the lower fraction there was obtained a few cubic centimeters, the odor of which suggested aldehydes. When it was allowed to stand in a bottle for ten days, considerable acid had developed—a great deal more than would have developed from an equal quantity of ether. The equivalent weight of the sodium salt of this acid was found to be 84.3 (sodium acetate, 82). From the low-boiling fraction obtained after redistillation there was obtained, on treatment with benzoyl chloride, *iso*-amyl benzoate; b. p., 250–255°. A portion of the distillate was saponified[4] with potassium hydroxide and from the potassium salt obtained the volatile acid was completely removed. A determination of the equivalent weight of the sodium salt made in the usual way gave 114.1 (sodium *iso*valerate, 124).

## Methylenediethyl Ether

The sample distilled from 86° to 89° and was free from acid and peroxide. After exposure for one year it had become 0.71 $N$ in active oxygen and 0.05 $N$ in acidity. It contained considerable hydrogen peroxide which was removed by repeated washing with water. The water extracts which contained both hydrogen peroxide and the ether peroxide, were acidified with a little sulfuric acid, warmed for several hours at 50° in a stoppered flask and then distilled. There was a strong odor of acetaldehyde and the latter substance was further identified by its characteristic behavior with ammoniacal silver nitrate and with potassium hydroxide solutions.

The peroxide was obtained as usual by the evaporation of small portions in a vacuum. The peroxide is completely volatile, leaving a small amount of residue which is not large enough to affect the results materially.

*Analyses.* Subs., 0.0458, 0.0570: 6.6 cc., 8.25 cc. of 0.1 $N$ sodium thiosulfate. Calc. for $C_5H_{12}O_4$: active O, 11.76. Found: 11.53, 11.58.

## Methylbenzyl Ether

This was prepared by the action of methyl alcoholic potassium hydroxide upon benzyl chloride, the former being in excess; b. p., 168–170°. A small sample was exposed for 24 hours at 85°, when it had become 1.2 $N$ in active oxygen. The main portion was exposed to diffused light at room temperature from July 1 to Nov. 15, when it had become 2.62 $N$ in active oxygen

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[4] All saponifications mentioned in this work were carried out in a narrow necked flask which was nearly filled and loosely stoppered. The reaction was carried out at 80°. It was desired to minimize the action of the air upon the ether.

and 1.2 $N$ in acidity. No benzoic acid had crystallized from the solution. The oxidized ether was shaken with water and considerable hydrogen peroxide removed which was estimated roughly to correspond to about 20% of the total active oxygen. There was no evidence of the presence of formic acid.

In another experiment, after three days' exposure the product had become 0.32 $N$ in active oxygen, while the acidity was negligible. A decided test for hydrogen peroxide was already obtained. At the end of two weeks the ether had become 1.36 $N$ in active oxygen and 0.04 $N$ in acidity. The relatively small amount of acid present in the earlier stages of the auto-oxidation is worthy of note. At this time, a part of the product was shaken with an equal volume of water to remove hydrogen peroxide, the amount of which was roughly estimated to represent about 7 to 8% of the total active oxygen, compared with 20% obtained in the previous experiment after four and a half months. The extracted ether was filtered and the filtrate heated for an hour at 130°. Only a trace of carbon dioxide was evolved but a small amount of methyl alcohol distilled. Nearly all of the ether peroxide was decomposed and considerable hydrogen peroxide remained. The main portion of the oxidized ether after a further exposure of ten weeks had become 4 $N$ in active oxygen. It was tightly stoppered and the bottle allowed to lie on its side while being exposed for the purpose of bringing about the decomposition of the peroxide. It was necessary to remove the stopper frequently to relieve the accumulated pressure. After three and a half months all of the peroxide had disappeared. Benzoic acid was found by titration to amount to about 11%. When the product was heated in an oil-bath to 150°, a small amount of methyl alcohol distilled which was converted into the *p*-nitrobenzoate; m. p., 94°. The residual oil was freed from benzoic acid by extraction with alkali. One cc. was then saponified with 1 g. of potassium hydroxide in alcohol in the usual manner. There was obtained 0.238 g. of benzoic acid (by titration) equivalent to 0.265 g. of methyl benzoate. The purified acid melted at 121°.

Another sample of ether[5] was found to oxidize slowly until it had been treated with alcoholic potassium hydroxide to remove chlorine derivatives. The purified product boiled at 165–168°. It was exposed for oxidation until it was 2.6 $N$ in active oxygen when it was shaken with water to remove hydrogen peroxide and with sodium bicarbonate solution to remove benzoic acid. To facilitate this treatment a little pure ethyl ether was added and subsequently removed in a vacuum. A portion of this purified product was allowed to stand for two months in a sealed tube; during this time considerable hydrogen peroxide and benzoic acid formed. Another portion was distilled in a high vacuum; the temperature of the bath was 55°. A residue was obtained which contained about 50% of the calcu-

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[5] Obtained from the Eastman Kodak Co.

lated ether peroxide. A dilute solution was obtained by shaking it with water and filtering. When a few drops of sulfuric acid were added and the solution allowed to stand for a day the peroxide was changed into benzaldehyde and hydrogen peroxide. The former was distilled and converted into the characteristic crystals of dibenzal acetone.

### Ethylbenzyl Ether

The ether was prepared in the same manner as the methyl compound; b. p., 183–185°. A sample exposed for oxidation in diffused light on April 4, reached a concentration of 3.75 $N$ in active oxygen by June 28; 35 cc. of this was mixed with a little pure ethyl ether and the mixture extracted with an equal volume of water. The extract contained 24% of the total active oxygen as hydrogen peroxide. It was partly distilled and the distillate again partly distilled. About 1 cc. of alcohol separated on the addition of potassium carbonate. The odor of acetaldehyde was noted. The aqueous residue from the first distillation was evaporated to about 5 cc. An abundant yield of succinic peroxide acid was obtained when the concentrated solution of hydrogen peroxide was shaken with 2 g. of succinic anhydride for $^3/_4$ hour.

The original sample of ether stood about three months longer during which time considerable benzoic acid crystallized and the strength in active oxygen decreased somewhat. The oil was extracted with sufficient sodium bicarbonate solution to remove all acid. A little pure ether was used in the extraction and subsequently it was removed in a vacuum at 50°. The product was exposed for decomposition which was complete in about two months. For each molecule of peroxide in the solution before the decomposition, there had developed about two-thirds of a molecule of free acid, which was nearly all benzoic. Forty cc. of the decomposed peroxide solution was shaken with an equal volume of water containing a little sodium sulfate to facilitate the separation. The water solution was filtered and distilled nearly to completion. The distillate was extracted with an equal volume of pure ethyl ether. The water now contained only 2% of the acidity of the original oil. This was neturalized with sodium hydroxide and the solution evaporated. When the residue of sodium salt was treated with strong sulfuric acid and warmed, the vapors of *acetic acid* were recognized.

The oil was then extracted with sodium carbonate solution to free it from benzoic acid and dried over calcium chloride. Practically all of it distilled between 182° and 200°. One cc. of the distillate was saponified with potassium hydroxide in alcohol with the usual precautions. From the amount of benzoic acid obtained it was calculated that the oil contained about 29% of ethyl benzoate by volume.

In stability, the ethylbenzyl ether peroxide in solution is similar to the methyl compound. Considerable decomposition takes place in amber glass but no noticeable pressure is developed. There is a little evolution of gas in diffused light. When heated at 120–130° for half an hour the peroxide was nearly all decomposed. A little alcohol distilled and a little hydrogen peroxide remained. Undoubtedly, the principal product of decomposition was ethyl benzoate.

### Dibenzyl Ether

The substance oxidizes at a rate comparable with that of the other two benzyl ethers. In time, benzoic acid crystallizes and a considerable proportion of hydrogen peroxide is present. The latter was removed by shaking with water and after the solution was concentrated it was converted into the easily identified succinic peroxide acid.

A portion of the oxidized ether which was about *N* in active oxygen was shaken with sufficient sodium bicarbonate solution to remove acid and hydrogen peroxide, a little pure ethyl ether having been added to facilitate the separation. The oil was filtered and heated at 45° in a vacuum for the removal of ether and water and then exposed for complete decomposition. The amount of benzoic acid formed was about a third of that of the original ether peroxide, molecule for molecule. The acid was removed by extraction with alkali and the oil then subjected to distillation in a good vacuum. A small proportion of relatively low-boiling distillate was obtained which was evidently a mixture of benzaldehyde and benzyl alcohol. The latter was dissolved with water and converted into the *p*-nitrobenzoic ester which after recrystallization from petroleum ether melted a little low, 80–82°. The benzaldehyde was identified by means of dibenzal acetone; m. p., 112°. On standing, the former was converted into a semisolid mass of benzoic acid.

### General

Both phenylmethyl and phenylethyl ethers showed no evidence of autooxidation. Allyl ethers develop peroxides much more rapidly than the corresponding hydrogenated derivatives; these peroxides decompose into resinous substances. The development of peroxide in ethylbutyl ether was found to be much more rapid than in methylbutyl ether, from which it is evident that the methyl group is unattacked.

Although the ethers are slowly attacked when completely removed from the light, yet the latter is a very important factor in the progress of the reaction. This is noticeable in the different results obtained in the summer and winter seasons. Oxidation takes place much more rapidly in the sunlight, although in most cases the peroxide does not accumulate. The final products appear to be the same in either case. It was shown previously that there is a progressive increase in the rate of oxidation of ethyl ether, which is due to acetaldehyde formed by hydrolysis of the peroxide. With the higher homologs above propyl ether such increase was not observed, this behavior being consistent with the fact that the peroxides were not found to undergo hydrolysis during the process of oxidation.

Ethyl ether peroxide was found to decompose to a considerable extent into carbon dioxide and methane. A similar decomposition takes place to a less extent with propyl ether peroxide. With the other peroxides, however, this reaction is negligible in amount and the principal decomposition results in the formation of acid and alcohol or ester. In all cases the acid formed consists largely of that which would be expected from simple oxidation of the alkyl group of the ether, for example, butyric acid from butyl ether. The reaction which results in the formation of formic acid is a minor one.

In three cases with normal ethers, where it was possible to remove the ether and other impurities by evaporation in a vacuum, peroxide residues have been obtained whose active oxygen content corresponds to the formula, $R_2O.O_2$. These results confirm the formula previously assigned to ethyl ether peroxide and make it appear very probable that the peroxidation of all ethers consists in the addition of one molecule of oxygen.

Since all the ether peroxides are hydrolyzed into aldehyde and hydrogen peroxide and also considering the nature of the principal acid formed by decomposition, the peroxides may be said to have the following formula, at least to a large extent, $R.O.HC(R')OOH$. The hydrolysis follows: $R.O.HC(R')OOH + H_2O = R'CHO + ROH + H_2O_2$. The decomposition of the peroxide may be represented thus: $R.O.HC(R')OOH \longrightarrow R'COOH + ROH$ or $R'COOR + H_2O$. The minor decomposition into formic acid may be explained thus: $R.O.HC(R')OOH \longrightarrow HCOOH + R'OR$.

The acids obtained with the aliphatic ethers have been found to be impure but whether this is due to an irregularity in the decomposition or to the presence of an isomeric peroxide in which the oxygen attaches itself to a different carbon atom, cannot be stated. The difficulty in obtaining any more definite knowledge concerning these substances lies in the fact that they cannot be purified by distillation or crystallization.

## Summary

Almost all ethers undergo peroxidation, which in the case of normal ethers consists in the addition of one molecule of oxygen to form an ether peroxide.

With *sec*-butyl ether the peroxide obtained is not a simple ether peroxide but is a derivative of acetone and hydrogen peroxide which results from the separation of *sec*-butyl alcohol.

The normal ether peroxides undergo spontaneous decomposition, especially under the influence of light, the principal products being acid and alcohol or ester.

Benzyl ethers are particularly easily oxidized, the peroxides being partly hydrolyzed into hydrogen peroxide, benzaldehyde and alcohols.

Detroit, Michigan

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

# THE ROLE OF WEIGHT OF ACYL IN THE MIGRATION FROM NITROGEN TO OXYGEN. I

By L. Chas. Raiford and C. E. Greider

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It has been shown[1] that when 2-acetylaminophenol is benzoylated by the Schotten-Baumann reaction, the benzoyl radical is attached to nitrogen while acetyl migrates to oxygen. In reporting these results attention was drawn to the fact that of the two acyl radicals thus far studied the heavier one was always found attached to nitrogen, regardless of the order in which they were introduced. It was suspected at the time, however, that factors other than the relative weights of the acyl radicals might be involved in the behavior observed, and it was explicitly stated that in the work already in progress an attempt would be made to determine whether the migration is dependent on the weights of the groups, their chemical characteristics,[2] or some consideration not yet noted. In the present work, however, it was desired to study the question of weight of acyl particularly, because the results thus far reported from this Laboratory do not agree with those obtained by Ransom[3] and extended by Ransom and Nelson,[4] in which it was found that the lighter of the two acyl radicals was always found on nitrogen.

In the work now reported the three aminophenols on which the first observations were made have been employed, and from them mixed diacyl derivatives were prepared by the use of the acetyl, benzoyl and $\alpha$-naphthoyl radicals. The $\alpha$-naphthoyl radical was selected because, in the first place, it is sufficiently heavier than benzoyl, so that it might be used not only to cause the migration of acetyl, but if weight alone were the

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[1] Raiford, This Journal, **41,** 2068 (1919).

[2] Beside the difference in weight between acetyl and benzoyl, the only radicals reported on in the preliminary paper, it was recognized that the difference in structure and acidity of these radicals might have a bearing on their behavior. In a report soon to be published, of which the experimental part has been completed, it will be shown that in the study of the mixed diacyl derivatives obtained by the successive introduction, in both possible orders, of thirteen pairs of radicals into a single *o*-aminophenol, 2-amino-4-methyl-6-chlorophenol, the chemical characteristic of the radical (dependent on composition and structure) may exert a very considerable and, in some instances, apparently decisive influence on the migration.

[3] Ransom, *Ber.*, **31,** 1060 (1898); **33,** 199 (1900); *Am. Chem. J.*, **23,** 1 (1900).

[4] Ransom and Nelson, This Journal, **36,** 390 (1914).