the reaction—at least in the case discussed here—exert a normal influence, whereby the unsaturated alcohol is obtained as the main product.

I might also mention here, that by following these conditions, we were able to improve the yields in unsaturated secondary alcohols from crotonaldehyde and alkylmagnesiumhalides.

Thus we have obtained 90% of the theoretical yields of penten-2-ol-4 and hexen-2-ol-4 from the aldehyde and methylmagnesiumiodide and ethylmagnesiumbromide, respectively.

Hydrolysis of Methyl-2-butyleneoxide-1,2.—10 g. oxide were boiled with 20 cc. water in a flask provided with a reverse cooler. The oxide layer began to decrease immediately and within 5 minutes disappeared completely. The oxide was, therefore, totally hydrated to the glycol, excepting for a minute quantity of methylethylacetaldehyde, which might have been present originally in the oxide.

Another sample of the oxide was left in contact with water at room temperature. The oxide layer had decreased in volume by only $^1/_3$ in 12 hours. Shaking would, naturally, increase the rate of hydration.

Conclusions.

Barbier-Grignard reactions with aliphatic ketones and aldehydes give better results if carried at low temperatures. Vigorous shaking is necessary to avoid local heating. This precaution is of absolute necessity in the case of substances containing mobile halogen atoms.

Organomagnesium reactions can be effected with the use of ethylchloride. The use of this substance is of especial advantage in the preparation of chloro-1-methyl-2-butanol-2, as the addition product between the alkylmagnesiumchloride and chloroacetone is quite soluble in ether.

In conclusion, I wish to express my thanks to R. B. Earle, for assisting me in these investigations.

CAMBRIDGE, MASS.

NEW PROCESSES FOR THE PREPARATION OF UNSATURATED HYDROCARBONS WITH CONJUGATED DOUBLE BONDS.

[FIRST PAPER.]

BY L. P. KYRIAKIDES.

Received February 2, 1914.

Pyrogenetic Decomposition of Oxides.

The most important representative of the butadiene-1,3 hydrocarbons is isoprene. This substance can be transformed to a rubber-like body, and is supposed to be the mother-substance of the natural product. Isoprene seems to have been first isolated by G. Williams, who also observes that "ozonized isoprene," on distilling off the more volatile portion, gradually becomes thicker, and finally, "the contents of the retort in-

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[1] *J. Chem. Soc.*, **15**, 110 (1862).

stantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers." Later, Bouchardat,[1] having treated isoprene in the cold with 12–15 parts of hydrochloric acid, saturated at 0°, and shaken the mixture occasionally in a sealed tube at ordinary temperatures during 15–20 days, isolated considerable quantities of a solid residue. This product was found to "possess the percentage composition of isoprene....and the elasticity and other characteristics of caoutchouc itself..... All of these properties seem to identify this polymer of isoprene with caoutchouc—the product from which isoprene is generated." Tilden[2] remarks that isoprene, obtained by the pyrogenetic decomposition of turpentine, formed rubber. The latter, he observes "appears to be produced most readily from the oily polymeride, resulting from the action of heat. Contact with strong acids in the cold effects the change."

The remarks of the above quoted authors led later investigators to study the conditions for the polymerization of isoprene to rubber. As a rule, however, their attempts failed to give any positive results. It was not until Fritz Hofmann of the Elberfelder Farbenfabriken, and Harries soon afterwards, succeeded in polymerizing isoprene to rubber, that polymerization was definitely established. Hofmann[3] and Harries[4] also observed that even the homologues of isoprene could be changed to rubber-like masses by the same process. Since the discovery of the last named investigators, a great amount of work has been carried out with a view to the synthetic production of the butadiene-1,3-hydrocarbons. The number of patents that have been issued in the last few years on the synthesis of these hydrocarbons is strong testimony to the importance of the technical production of rubber. The writer does not intend to enter into any discussion as regards the relative merits of these patents, either from a scientific or technical point of view. A good many of the patents, in my estimation, have no practical value at all; while others, being merely the result of theoretical reasoning, could not be carried out in practice.

Isoprene, $CH_2 : C(CH_3).CH:CH_2$.—α-Oxides, when passed through glass tubes heated at 500°, undergo a metamerization, giving rise to aldehydes or ketones, or both, depending on the molecular structure of the oxides. Ipatieff and Leontovitch,[5] who first studied these pyrogenetic reactions, observed also that heated catalysts, such as aluminum oxide, effect the metamerization of the α-oxides at a much lower temperature. These investigators obtained a mixture of methylisopropylketone and

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[1] *Compt. rend.*, **89**, 1118 (1879).

[2] *J. Chem. Soc.*, **45**, 415 (1884).

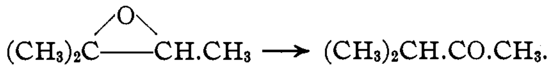
[3] *Chem. Zentr.*, **1911**, II, 175, 176.

[4] *Ann.*, **383**, 190, 210 (1911).

[5] *Ber.*, **36**, 2016 (1903).

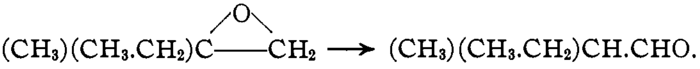
methyl-1-butyraldehyde, by passing trimethylethyleneoxide, which contained some of the isomeric substance, methyl-2-butyleneoxide-1,2 over aluminum oxide at 250–260°. These reactions took place as follows:

(1)



$$(CH_3)_2C\overset{O}{\frown\!\!\!-\!\!-}CH.CH_3 \longrightarrow (CH_3)_2CH.CO.CH_3.$$

(2)

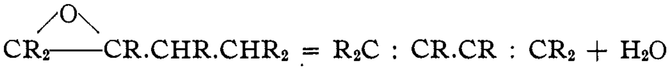


$$(CH_3)(CH_3.CH_2)C\overset{O}{\frown\!\!\!-\!\!-}CH_2 \longrightarrow (CH_3)(CH_3.CH_2)CH.CHO.$$

Ipatieff and Leontovitch have also observed that amylene oxide, passed through a glass tube heated at 600°, suffered partial decomposition. At this temperature (in absence of aluminum oxide) they obtained, besides the ketone and aldehyde, a mixture of gases consisting of saturated and unsaturated hydrocarbons, hydrogen, carbon monoxide and dioxide. This metamerization of oxides to ketones or aldehydes is also readily effected at much lower temperatures by substances having an acid reaction.

One of the best known methods for preparing olefins is by the dehydration of saturated alcohols by substances known generally as dehydrating catalysts, such as the oxide, silicate of aluminum, etc. These reactions have been studied by Ipatieff, Sabatier, Senderens and others.[1]

In June of 1911, I discovered that oxides can be dehydrated to the corresponding diolefines with conjugated bonds, according to the following scheme:



$$CR_2\overset{O}{\frown\!\!\!-\!\!-}CR.CHR.CHR_2 = R_2C : CR.CR : CR_2 + H_2O$$

where R may be a hydrogen atom or an organic radical. It will be seen that this dehydration is similar to that of the saturated alcohols, as in both cases one molecule of water is split off from each molecule of the substance brought into reaction.

The methyl-2-butyleneoxide-1,2 used in the following experiments was prepared from chloro-1-methyl-2-butanol-2. The latter substance was obtained, as described in the previous paper, by the action of methylmagnesiumhalide on chloroacetone:

Experiment 1.—Fifty grams of the oxide were passed through a glass tube heated at about 400° and containing a layer of aluminum silicate in the form of fine powder. The length of the silicate layer was about 50 cm. The oxide was introduced into the tube in drops, and the distilling substance collected in a receiver cooled with ice and salt. The distillate was separated from the water, dried over calcium chloride, and fractioned through a column. Eleven grams of the liquid distilled over between 30–45°, and 20 g. distilled over at 80–95°, mostly about 90°.

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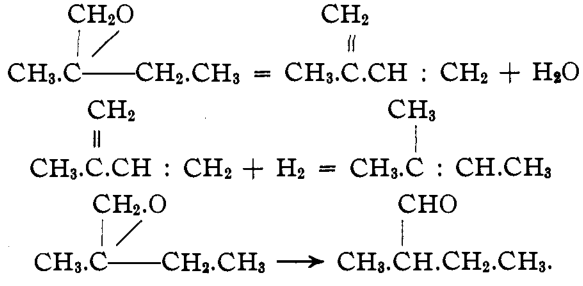
[1] *Lehrbuch der Org. Chemie*, Meyer and Jacobson, Second ed., 1, I, 817–818.

This latter substance consisted of impure methyl-1-butanal, formed by the metamerization of the oxide, as previously observed by Ipatieff and Leontovitch. The liquid boiling at 30–45° was refractioned, and the portion boiling between 30–40° (mostly 33–38°) was dissolved in ether, cooled in ice, and treated gradually with bromine. The brominated compound was found to consist of approximately equal amounts of trimethylethylene and isoprene dibromides.[1] Trimethylethylene could not have been formed normally from the oxide, as the dehydration product could be only a hydrocarbon containing two double bonds. And as will be seen later, isoprene being the normal dehydration product of the oxide, trimethylethylene could have been only formed by the secondary reduction of the isoprene.

Now, it is found that during the pyrogenetic catalysis of the oxide, the catalyst is soon covered with a layer of carbon, so that its activity steadily decreases and eventually stops altogether. The result of this is, that, as carbonization progresses, the relative amounts of methylethylacetaldehyde(methyl-1-butanal) distilling over increase, and towards the end the only result of the distillation of the oxide over the catalyst is a simple metamerization of it to the aldehyde. Carbonization is also evidence of a more or less general decomposition of the carbon chain, resulting in the formation of gaseous products. These may be similar in nature to those observed by Ipatieff and Leontovitch in the case of the mixture of amylene oxides. Hydrogen being one of these decomposition products, it stands to reason that isoprene is reduced by it to trimethylethylene. The three main reactions in the dehydration of methylbutylene oxide may be represented as follows:



(1)

(2) $$CH_3.\overset{\overset{\displaystyle CH_2}{\|}}{C}.CH : CH_2 + H_2 = CH_3.\overset{\overset{\displaystyle CH_3}{|}}{C} : CH.CH_3$$

(3)

Commenting on the pyrogenetic decomposition of turpentine to isoprene, Harries and Gottlob[2] observe that they obtained varying yields of the hydrocarbon, depending on the dipentene contained in the commercial product. Staudinger and Klever,[3] on the other hand, observe that by

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[1] The boiling point of isoprene dibromide is 92° at 12 mm.; 105° at 20 mm.; 119° at 42 mm.

[2] *Ann.*, 383, 229 (1911).

[3] *Ber.*, 44, 2212 (1911).

decomposing terpene hydrocarbons *in vacuo* they could increase the yield of isoprene. They effected this depolymerization by means of an electrically heated platinum spiral. By reducing the pressure within the apparatus to 2–3 mm. they obtained as high as 60% yield of very pure isoprene. In the older pyrogenetic decompositions of turpentine, where the reaction was carried out at ordinary pressures, the "isoprene" contained appreciable amounts of trimethylethylene.

The above consideration led me to study the effect of reduced pressure on the catalysis of the oxide. The results were found to agree with the expectation.

Experiment II.—Ninety-nine grams of methylbutyleneoxide were slowly distilled through a glass tube containing freshly prepared and ignited pieces of kaolin. The latter filled the tube over a length of 60 cm. The temperature of reaction was kept at 440–460°. The pressure within the apparatus was reduced to about 60 mm. The decomposition products were passed first through a receiver cooled with ice water, and the low boiling liquids condensed in a second receiver cooled with a mixture of solid carbon dioxide and ether. The water formed from the dehydration amounted to 18 cc., which is equivalent to 86 g. of the oxide. The organic substances were dried and fractioned through a column. Forty-nine g. of the substance boiled below 45°, mostly at 33–38°, 12 g. of the oxide were recovered as methylbutanal. The yield of the hydrocarbon fraction amounted to about 62% of the total oxide used. But, as the water of dehydration amounted to 87% of the theoretical, it is very likely that quite a little of the hydrocarbon fraction was lost, partly during the catalysis, and partly in handling it prior and during the fractionation. Considering, now, that methylbutanal also can be dehydrated to isoprene, it is quite natural to assume that the dehydration of methyl-2-butyleneoxide-1,2 can be made very nearly quantitative.

The metamerization of the oxide to the aldehyde is a function, among other things, also of the rate of catalysis; hence the slower the dehydration, within certain limits, the less will the amount of aldehyde obtained be. The catalyst in the experiment was found to have been much less carbonized than the one in the preceding experiment. This would indicate that the amount of trimethylethylene formed would be much less. This was proven to be the case by separating the two hydrocarbons by means of their dibromides, as above. Thus it was found that the mixture of the dibromides consisted over 80% of the isoprene derivative. The isoprene dibromide was dehalogenated to the hydrocarbon by Gustavson and Demjanoff's[1] zinc-dust method, and the isoprene polymerized to rubber. The purified rubber as well as the vulcanized product were found to be of good quality.

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[1] *Chem. Zentr.*, 1888, 1345.

Experiment III.—One hundred grams of the oxide were dehydrated as in the last experiment with kaolin at 450°. The pressure was kept at below 1 mm. by means of a May-Nelson rotary vacuum pump. No attempt was made to get a quantitative catalysis, as the pump leaked a little. The decomposition products were collected at ordinary pressures at the exit end of the pump. Thirty grams of the dried liquid boiled at 34–37°. The high boiling fraction consisted mostly of methylbutanal. The hydrocarbon was dried over night in presence of sodium. In the morning it was found that some of the isoprene had already solidified. The unchanged hydrocarbon was distilled into a sealing tube—the hydrocarbon showed an absolutely constant boiling point of 35–36°. The liquid was treated with 1–2 g. of sodium wire, and after sealing the tube, submitted to polymerization according to Harries'[1] directions. The tube was kept at 60° for two hours, and then left at room temperature over night. In the morning the contents of the tube were found solid, except a little portion on the surface, which showed signs of a slight mobility. The heating at 60° was continued for about 16 hours more. The rubber was treated according to the directions of Harries, and, after drying, weighed 12 grams. The product was very tough, and was vulcanized to a substance having more of the properties of leather than of vulcanized natural rubber. It has been observed by Harries[2] that the sodium polymerization products are not identical with the "normal" polymerization products, hence it is not surprising if the vulcanized products in this case had different physical properties.

Harries,[1] discussing the polymerization of isoprene in presence of sodium, states that the best results are obtained with the pure hydrocarbon. In this case, it can be polymerized quantitatively to a solid, rubber-like mass, on heating for 50 hours at 60°. It would seem, therefore, that the isoprene obtained in experiment 3 was as pure as could possibly be obtained, as this latter product required considerably less time to solidify than the product obtained by Harries and Gottlob from carvene on decomposing the latter by means of the "isoprene-lamp." It has been our experience that impure samples of isoprene never gave a good sample of rubber. It follows, therefore, that the hydrocarbon, obtained by the older pyrogenetic depolymerization methods of terpenes at ordinary pressures, must be separated from the accompanying trimethylethylene before it is subjected to polymerization.

Staudinger, Endle and Herold,[3] in a recent paper, discuss the pyrogenetic decomposition of butadiene hydrocarbons, and observe that isoprene, passed through a tube heated at 750°, is changed partly to tarry

[1] *Ann.*, 383, 217 (1911).

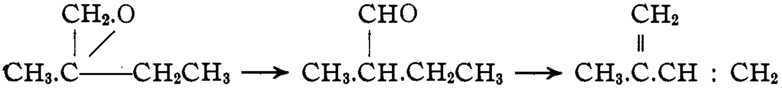
[2] *Ibid.*, 383, 210, 217, 221; 395, 221, 244, 245, 253.

[3] *Ber.*, 46, 2466 (1913).

substances. The rest is broken up into gaseous products, such as butadiene, hydrogen, methane and ethylene. The formation of these is accompanied by considerable carbonization. Even at 400–500° isoprene undergoes partial change, as it was found that trimethylethylene was formed to some extent by the reduction of the isoprene. The same authors also observe that isoprene can be distilled several times over a glowing platinum spiral at 15 mm. without suffering any considerable transformation.

The conclusion from the experiments above described, and the work done by the last named authors, is that any pyrogenetic reactions for the production of isoprene or its homologues must be carried out under low pressure.

Dehydration of Methyl-1-butanal, $CH_3.CH_2.CH(CH_3).CHO$.—It has been observed that isoamylene oxide in the course of its dehydration to isoprene is partly metamerized to methylbutyraldehyde. Considering the work of Ipatieff and Leontovitch,[1] one might be led to assume that the dehydration to isoprene is a secondary process, the first being a metamerization of the oxide to the aldehyde—this taking place at about 250° in presence of a catalyst. If this assumption were true, the reactions involved would take the following course:



The methylbutanal used was obtained by the fractionation of the crude aldehyde fractions formed in the catalysis of the oxide.

One hundred g. of the aldehyde were catalyzed as in Experiment 3. The temperature was kept at 500–550°, and the vacuum was that of the May-Nelson pump. The dried decomposition products were fractioned through a column; 10 g. of the substance boiled at 34–39°. This product was dried over sodium, and distilled into a sealing tube. It was polymerized by Harries' sodium method. The liquid took a long time to show signs of thickening, and it was only after months' standing, that it set to a rubber-like mass. This slowness of polymerization must have been due to the impurity of the hydrocarbon.

The dehydration of the aldehyde is accompanied by considerable carbonization, which soon stops the activity of the catalyst. Having attempted to dehydrate methylbutanal to isoprene a number of times, I am inclined to think that the dehydration of the oxide is a direct process, and is much easier, and gives a purer product than the aldehyde. It is also observed that the reaction with the oxide is effected at lower temperatures.

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[1] *Ber.*, 36, 2016 (1903).

Conclusions.

Oxides of the hydrocarbons can be dehydrated to the hydrocarbons of the butadiene series, at temperatures above 350° and in presence of catalysts.

The use of reduced pressures in these reactions is absolutely necessary; otherwise, the butadiene hydrocarbon suffers partial decomposition, giving rise, among other products, to hydrocarbons with one double bond. The hydrocarbons obtained with the use of high vacuum can be polymerized directly after distillation.

Methyl-1-butanal is capable of dehydration to isoprene.

In conclusion, I wish to thank my colleague, R. B. Earle, for helping me in carrying out the experiments described in this paper.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ACTION OF HALOGEN ON 4-NITRO-*m*-CRESOL.

BY L. CHAS. RAIFORD.

Received February 10, 1914.

In their proof of the position of the chlorine atom in the stereoisomeric oximes which they obtained from para chlorotoluquinone, Kehrmann and Tichvinsky[1] started out by chlorinating 4-nitro-*m*-cresol.[2] They obtained a product which they regarded as a monochloro compound, in which they assumed that chlorine had taken a position para to methyl. Without isolating their product, they reduced it to the corresponding aminocresol, which latter they reported as identical with the monochloroaminocresol obtained by the reduction of their oximes. In addition to the fact that, in the experiments cited, the intermediate products were not isolated, proof of the position of chlorine is further lacking to the extent that the oximes were not prepared from the base obtained by reduction of the chloronitrocresol; nor was it shown that this base could be oxidized into the quinone from which the oximes were prepared. The identity of the bases obtained from the two sources was claimed solely on the fact that they melted at the same temperature, and that their acetyl derivatives had identical m. p. It is not stated whether the corresponding products were melted together or not.[3]

The present writer, working with Stieglitz, in an attempt to prepare

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[1] *Ann.*, **303**, 20 (1898).

[2] *Ibid.*, **217**, 52 (1883).

[3] I have recently found that 6-chloro-4-amino-*m*-cresol (OH = 1), the base obtained by the reduction of Kehrmann's oximes, in the condition in which he obtained it, m. p. 206–207°, may be melted with 5-chloro-4-amino-*o*-cresol, m. p. 205–206°, without depression. This indicates that it would be unsafe to assume the identity of two products, in this class, at least, without evidence other than that obtained by melting them together.