ylene homologue. The hydrocarbon boiling at 78–82° weighed 40 g. The theoretical yield would be 72 g. Reif[1] gives the boiling point of this hydrocarbon as 80–82°; while, according to the "Lehrbuch,"[2] hexadiene-2,4 boils at 87–89°. The water of dehydration in this experiment amounted to 17 cc., instead of the theoretical 18 cc. Another sample of hexenol was decomposed at ordinary pressures. From 390 g. alcohol 190 g. of a liquid boiling between 76–86° was obtained. This was refractioned, and 145 g. of the hydrocarbon were collected at 80–84°. In the dehydration of pentenol and hexenol prepared from crotonaldehyde it is observed that there is always a fraction among the decomposition products, which boils below 30°, and has the smell of acetaldehyde. This latter substance is formed from the paraldehyde which is always present in the crotonaldehyde.

An attempt was made to dehydrate hexen-2-*ol*-4 by means of crystallized oxalic acid. Fifty grams of the alcohol were heated at 110° with 40–50 g. of the acid. The decomposition products were dried and fractioned as usual through a column. 7 g. of these boiled at 78–83°. Most of the hydrocarbon, however, was found in a polymerized condition floating over the oxalic acid. These polymerization products smelled strongly of terpene-like substances.

Conclusion.

Glycols and unsaturated alcohols can be dehydrated to divinyl hydrocarbons. The decomposition is improved by using reduced pressures during the pyrogenetic dehydration at temperatures above 350°.

Ditertiary α-glycols seem to be capable of dehydration to the *diene-1,3* hydrocarbons in presence of freshly reduced and finely divided catalytic metals. This reaction is made to take place at temperatures above 400°.

I would like to express, here also, my indebtedness to R. B. Earle for assisting me in these investigations.

CAMBRIDGE. MASS.

NEW PROCESSES FOR THE PREPARATION OF BUTADIENE-1,3 HYDROCARBONS. III. CATALYTIC DEHYDRATION OF HYDROXYL-COMPOUNDS.

BY L. P. KYRIAKIDES.

Received March 4, 1914.

Part I. Dehydration of Ditertiary Glycols.

Pinacone, a ditertiary α-glycol, has been subjected to a great many reactions which are characteristic of substances containing hydroxyl groups. Whereas this glycol[3] is quite stable when heated to fairly high

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[1] *Ber.*, 41, 2744 (1908).

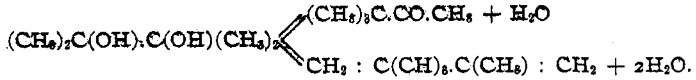
[2] Organ. Chemie, Meyer-Jacobson, 2nd ed., Vol. I, Part I, pp. 887.

[3] Vorländer, *Ber.*, 30, 2266 (1897).

temperatures in presence of alkaline compounds, such as a solution of sodium carbonate, it is very readily attacked by acids or dehydrating agents to give rise to pinacoline. The halogen-hydrin and the dihalogen esters of pinacone are more or less readily obtained by the action of the halides of phosphorus in the cold. The action of halogen acids, on the other hand, is dependent on the character of the acid, its concentration, the nature of the solvent and also on the temperature of reaction. Baeyer[1] has obtained the dibromide by treating anhydrous pinacone with a saturated solution of hydrobromic acid in acetic acid. Kondakoff[2] has prepared the dichloroester by treating the glycol at ordinary temperatures with an aqueous solution of hydrochloric acid saturated at —20°; or by saturating pinacone at —10° with hydrochloric acid gas and leaving the reaction mixture at ordinary temperatures for several days. In every instance, however, there is an appreciable amount of pinacoline formed. Kondakoff observes also that there is less pinacoline formed "the more concentrated the hydrochloric acid used is, and the more carefully heating during the reaction is avoided." Harries[3] reports that, when a strongly cooled chloroform solution of anhydrous pinacone is saturated with dry hydrochloric acid gas, a quantitative separation of a crystalline substance takes place, which is very sensitive to the action of air. This substance was found to consist of the monohydrochloride of pinacone, an addition product, and is said to be very unstable, decomposing even at 55° with evolution of hydrochloric acid gas.

Dimethyl-2,3-butadiene-1,3, $CH_2 : C(CH_3).C(CH_3) : CH_2$.— Couturier[4] has observed that dilute sulfuric acid reacts with pinacone to give rise to small quantities of dimethylbutadiene, the main decomposition product being pinacoline.

Kondakoff[5] has carried out this reaction by heating pinacone with 10% sulfuric acid, and obtained, besides the two products mentioned by Couturier, also a fraction of high boiling point. The main reactions in Couturier's process take place as follows:



$$(CH_3)_2C(OH).C(OH)(CH_3)_2 \begin{cases} (CH_3)_3C.CO.CH_3 + H_2O \\ CH_2 : C(CH)_3.C(CH_3) : CH_2 + 2H_2O. \end{cases}$$

Couturier[6] has also obtained the hydrocarbon in small quantities by heating pinacone with acetic anhydride in sealed tubes. Kondakoff,[7] on the other hand, prepared the same hydrocarbon by heating the dibrom-

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[1] *Ber.*, 26, 2563 (1893).

[2] *J. prakt. Chem.*, 62, 169 (1900).

[3] *Ann.*, 383, 183 (1911).

[4] *Ann. chim. phys.*, 26, [6] 485 (1892).

[5] *J. prakt. Chem.*, 62, 173 (1900).

[6] *Ann. chim. phys.*, 26, [6] 457–458 (1892).

[7] *J. prakt. Chem.*, 62, 170.

ide of pinacone with alcoholic potassium hydroxide at 130–140°. These investigators have noted that β,γ-dimethyldivinyl is easily polymerized. Kondakoff,[1] furthermore, discovered that part of the hydrocarbon, after heating it at 150° for 5 hours with alcoholic potassium hydroxide, was polymerized to a product whose "properties remind one of those of rubber or of the polymers of styrol." The solid product "consists of a leather-like, elastic mass of an almost white color, which is not volatile with steam, is insoluble in water; but is soluble in hydrocarbons, ether and alcohol." In a later paper,[2] the same investigator reports briefly the results of further experiments on the polymerization of diisopropenyl. He sealed two samples of the hydrocarbon; one sample was prepared from pinacone by Couturier's sulfuric acid method, while the other was prepared by Kondakoff's own method by the dehalogenation of the dibromo-ester of pinacone with alcoholic potassium hydroxide. The former preparation had been fractioned over sodium. The tubes containing the hydrocarbon were left in diffused light for one year, at the end of which period both samples of the hydrocarbon were found to have solidified *completely*. Kondakoff states that the substance is amorphous and elastic like rubber, that it does not dissolve in the ordinary organic solvents, and only "swells up in benzol." He also mentions that the product obtained in this case must have been a higher polymerization product as compared with the one obtained by the action of alcoholic potassium hydroxide at 150°, hence the difference in solubility in the ordinary solvents. I have reproduced here the most important parts of Kondakoff's reports in support of his claim of having definitely proven that diisopropenyl at least could be made to polymerize to a rubber-like substance. Attempts have been made recently to discredit this claim of Kondakoff, on the ground that the products obtained by him are not to be regarded as true rubber, because the decomposition curves[3] of the diozonides of the "normal rubber" and the substance obtained by Kondakoff showed great variations. In justice, however, to Kondakoff be it said that he was able, as early as 1900, to observe a certain relation between his products and rubber, as there is undoubtedly some relation between them. It has been our experience that, with the possible exception of divinyl, the β,γ-dimethyl derivative seems to be the easiest to polymerize to a rubber-like substance by the action of heat and catalysts. By treating this hydrocarbon with 1% its weight of a catalyst and heating the mixture in metal receivers for three weeks at 100–115°, we have been able to obtain as high as 80% yield of a very tough and fairly elastic "rubber." The physical properties of this "rubber" vary considerably with the temperature and duration of polymerization, as would be expected.

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[1] *J. prakt. Chem.*, **62**, 175–176.

[2] *Ibid.*, **64**, 109 (1901).

[3] Harries, *Ann.*, **395**, 265 (1913).

The fairly high boiling point of dimethylbutadiene, its ease of polymerization, and its preparation from pinacone, which can itself be directly obtained by the reduction of acetone, make the study of the hydrocarbon both interesting and highly desirable. A great many patents have appeared during the last few years dealing with the dehydration of pinacone to the hydrocarbon. One of the most important of the processes,[1] patented by the Badische Anilin Fabrik of Germany, is the pyrogenetic decomposition of the glycol by dehydrating catalysts. A great many patents have been granted to the Elberfelder Farbenfabriken,[2] which are based on improvements of Couturier's method for the dehydration of pinacone in the wet way by heating it with dilute sulfuric acid. The chemists connected with this firm have discovered that the yields of hydrocarbon increase as the amount of the acid is diminished, in fact, by using traces of the acid they have been able to obtain as high as 70% of the theoretical yield of diisopropenyl. The same investigators have also generalized this observation so as to include the organic sulfonic acids. Furthermore, they have observed that acid salts of sulfuric acid such as potassium bisulfate, and normal sulfates which react acid, can also be used in effecting the dehydration of pinacone to the hydrocarbon.

In view of the work reported in this paper, the decomposition of glycols and alcohols to hydrocarbons in the wet way is not a simple dehydration in the usual sense of the expression in that it is produced by substances known generally as dehydrating agents, such as sulfuric, phosphoric and oxalic acids or zinc chloride. It is my belief that the dehydrations mentioned here are the result of a previous esterification, and are effected only by acids having a high ionization constant. Phosphoric and oxalic acids, weak acids,[3] which are usually spoken of as strong dehydrating agents, transform pinacone to pinacoline. Halogen acids, on the other hand, are not usually known as inducing the dehydration of alcohols or glycols. Being strong acids, they are well suited for esterification purposes, as is known to every one. These acids, as will be described soon, have been discovered to be capable of catalyzing hydroxyl substances to the hydrocarbons under certain conditions. These halogen acids, and especially hydrobromic and hydriodic acids, being susceptible of greater dissociation, are perhaps better adapted for the catalytic decomposition of pinacone to the hydrocarbon than straight sulfuric acid. It has been observed[4] that the halogen esters of pinacone are only obtained if the glycol is treated *in the cold* with concentrated halogen acids, and that warming of the liquid

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[1] D. R. P. 235,311; *Chem. Zentr.*, 1911, II, 112; Fr. Pat. 417,275; *C. A.*, 6, 2548 (1912). (The abstract in the *C. A.* needs correction. The French word "Alumine" has been translated "Aluminum" instead of *Alumina*—aluminum oxide.)

[2] U. S. Pat. 1,002,399, 1,002,400; *Chem. Zentr.*, 1912, II, 776, etc.

[3] Vorländer, *Ber.*, 30, 2266 (1897).

[4] Compare also Delacre, *Bull. soc. chim.*, [4] 3, 204 (1908).

in presence of the excess of acid induces the formation of increasing quantities of pinacoline. We have discovered, however, that if pinacone is heated with very small amounts of any highly ionized acid, other than sulfuric acid and its derivatives, whose action was studied by the German chemists as noted above, the yield of hydrocarbon is very good. Acids, such as nitric acid which induce secondary reactions as oxidation, are not suited for the catalysis of hydroxyl compounds. The pinacone used in the following experiments was prepared by distilling the hydrate through a column until the temperature of the vapors attained 115°, and the residue was taken as practically anhydrous glycol.

Experiment 1.—Five hundred grams pinacone are put in a flask carrying a two-hole stopper one of which is fitted with a dropping funnel and the other with a fairly tall Young's column. The column is provided with a thermometer. The glycol is treated with 1–2 g. of hydrobromic acid solution (48%), and the mixture heated to boiling over a wire gauze. The heating is so regulated that the decomposition products distilling through the column do not register a temperature higher than 92°.

The reaction is carried out at constant concentration of the catalyst by dropping in fresh pinacone through the dropping funnel. This reaction lasts for quite a long time. In case it is observed to slow down, a fraction of a gram of hydrobromic acid is added and the decomposition of the glycol continued as long as desired. The slowing down of the reaction is due to the fact that some of the acid is gradually carried over by the distilling vapors, as was determined by testing the aqueous layer of the distillate. Two grams of the hydrobromic acid solution are capable of decomposing over 500 g. pinacone. The distillate is separated from the aqueous layer and the crystals of pinacone hydrate (pinacone is very volatile with steam) shaken twice with fresh water, dried over calcium chloride or potassium carbonate, and is finally fractioned through a column. The fraction boiling below 90° is refractioned, and the liquid boiling at 69–71° is collected as dimethyl-2,3-butadiene-1,3. The yield of hydrocarbon in this case was over 70% of the theoretical. The by-products of the reaction are mainly pinacoline, and a small amount of a liquid of high boiling point, which deposits big prismatic crystals on standing. The nature of the latter liquid and the crystals were not determined. *Hydrochloric acid* does not react well, which may be due to the relative ease with which it is volatilized, as can be proven by testing the distillate. In using this acid the reaction can be made to continue by the frequent addition of the acid, which, however, induces the formation of greater quantities of pinacoline. *Hydriodic acid* is as good a catalyst as hydrobromic acid. By treating 50 g. of pinacone with 5–7 drops of hydriodic acid solution, and carrying out the distillation of the decomposition products at constant concentration of the acid, I was able to obtain about 70% of the theoretical yield of dimethylbutadiene. *Trichloroacetic* acid is one of the strongest organic acids, its dissociation constant approaching that of the *strong* inorganic acids.

Experiment II.—Twenty-five grams of pinacone were put in a small flask, the apparatus being similar to the one used in Experiment 1, and the glycol decomposed by the action of about 1 g. trichloroacetic acid at 170–180°. The flask was heated in an oil bath. A good way to determine the amount of catalyst necessary to effect a fairly rapid decomposition is to heat the pinacone and to add the catalyst in small portions until a smooth reaction sets in, care being taken to avoid introducing an excess of the catalyst, otherwise the tendency will be in the direction of the formation of pinacoline.

The decomposition products, in this case, distilled over at about 90°. The reaction was not of long duration, hence I had to add fresh trichloroacetic acid at frequent intervals. The decomposition of 25 g. pinacone required about 4 g. of the acid. The action of trichloroacetic acid may be due to the hydrochloric acid set free by the decomposition of the organic acid at the relatively high temperature of reaction. This view is supported by the fact that testing the water of dehydration with silver nitrate gave a flocculent precipitate, which was evidently silver chloride. The purified hydrocarbon amounted to about 50% of the theoretical.

The fact that highly ionized acids induce the decomposition of pinacone in the wet way to the hydrocarbon has led us to assume that the salts of these acids with weak alkaline substances would react similarly. It is a matter of general knowledge that such salts react acid. It would follow, therefore, that the acid liberated after dissociation would play the role of catalyst. The weaker the base in combination with the acid, the more active will the salt be. Among such salts might be mentioned the aniline salts of the halogen acids. Nernst,[1] in a table of the affinity constants of the weak bases, gives the constant for the aniline base—$NH_3(C_6H_5)OH$—as $K10^6 = 0.00011$, as compared with ammonia, whose constant is given as $K10^6 = 23$. The affinity constants are directly proportional to the dissociation constants. It is evident that the aniline base is a much weaker base than ammonia, which is itself known as one of the weak bases. Because of this fact, the halogen acid salt of aniline reacts like the free acid.

Experiment III.—1.5 kilo pinacone were introduced in a 2-liter flask provided with a column and a dropping funnel. The glycol was then treated with about 20 g. aniline hydrobromide and decomposed by heating the flask on a wire gauze. The heating was regulated so that the vapors of the decomposition products registered a temperature of about 90° and the concentration of the catalyst was kept constant by dropping in fresh pinacone. Twenty grams of aniline hydrobromide were sufficient

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[1] Theoretical Chemistry," English translation, 6th ed., p. 512.

to catalyze more than 3 kilos of the glycol. The reaction can be continued indefinitely by adding small quantities of the salt or of the acid in case it is observed to slow down. This reaction is very smooth and ideal for laboratory as well as technical purposes. The distillate was treated as under Experiment I, and we obtained over 70% of the theoretical yield of dimethylbutadiene.

Experiment IV.—Twenty grams of pinacone were heated and treated with small portions of anhydrous ferric chloride until a fairly smooth reaction had set in. It was found necessary to add fresh salt at frequent intervals, otherwise the reaction had a tendency to stop. Ferric hydroxide accumulated in the reaction flask, while the hydrochloric acid kept distilling over with the decomposition products. The purified hydrocarbon amounted to about 35%, the rest being mostly pinacoline.

Experiment V.—Twenty grams of pinacone were heated and treated gradually with small quantities of anhydrous aluminum bromide until the glycol began to be decomposed smoothly. The apparatus was similar to the one used in all these experiments. The reaction, as was expected, was found to be comparable with the straight hydrobromic acid catalysis. In this case aluminum hydroxide precipitates out of the reaction mixture. The decomposition was carried out as usual at constant volume by the introduction of fresh pinacone. In view of the above-mentioned behavior of the salts of the halogen acids with weak bases, it occurred to me that even some of the halogen esters of alcohols and glycols might act similarly. It is known, that the tertiary groups are characterized by their great mobility, and that the tertiary esters are easily hydrolyzed liberating the free acid; they also suffer partial decomposition at high temperatures, whereby the halogen acid is again set free.

Experiment VI.—Fifty grams pinacone were treated with a fraction of a cubic centimeter of trimethylethylene dibromide, which was freshly prepared by shaking it with a solution of sodium carbonate, drying and carefully fractioning *in vacuo*. The mixture was heated as usual, and the decomposition products worked up for the hydrocarbon. The yield of dimethylbutadiene was about 35%. It may be possible to regulate the relative quantities of these catalysts so as to obtain a maximum yield of the hydrocarbon. However, there is always a concentration of the catalysts below which no reaction takes place; while on the other hand, and this is true of the ditertiary α-glycols, when the concentration of the catalyst reaches beyond a certain maximum, the tendency is in the direction of pinacoline formation.

Part II. Dehydration of Secondary-Tertiary and Disecondary Glycols.

I. Methyl-2-pentadiene-2,4, $(CH_3)_2C : CH.CH : CH_2$.—This hydrocarbon is of especial interest, because it is, perhaps, the easiest of all the *divinyl* hydrocarbons to synthesize. Its physical constants are such as to make its handling a matter of the greatest simplicity. Comparing this hydrocarbon with its isomer dimethyl-2,3-butadiene-1,3, we find that the new hydrocarbon has a higher boiling point, and that its preparation is simpler and the yields more nearly quantitative. The starting point in the synthesis of both hydrocarbons is acetone. The new hydrocarbon is obtained as follows: Acetone is condensed to diacetone alcohol, the latter is reduced to the corresponding glycol, and this is finally dehydrated directly to the hydrocarbon. The yields in each step can be made very nearly quantitative. For the condensation of the ketone to diacetone alcohol see Hoffman,[1] and my paper on "Organic Preparations." Diacetone alcohol can be easily reduced to the glycol in a number of ways. By reducing it electrolytically we have obtained as high as 70% of pure glycol from a crude sample of diacetone alcohol. Zelinsky and Zelikoff[2] have reduced the ketone alcohol in fairly dilute aqueous solution with a 3% sodium amalgam, and have obtained 87% of the theoretical yield. The side-products formed in each step are comparatively small in amount. The reduction, on the other hand, of acetone to pinacone is not as readily effected. The electrolytic methods[3] do not give good results. The use of magnesium and aluminum[4] amalgams necessitates the increase in the cost of production, and the side products formed are appreciable in quantity. Besides, there is the problem of handling these side products, the working back of the metal oxides and the recovery of the mercury which necessarily would tend to make the process more complicated. There is also this point to be remembered, that the decomposition of pinacone is not as quantitative a reaction as that of its isomer, methyl-2-pentandiol-2,4. This latter glycol was used in the following experiment, and was prepared by the electrolytic reduction of diacetonealcohol.

Fifty grams of the glycol were catalyzed as usual by heating it with about 1 g. aniline hydrobromide. The mixture was heated at such a rate that the products distilling through the column registered a temperature below 95°. 240 g. more glycol were dropped in, and the decomposition finally carried to an end, until a few cubic centimeters only were left in the flask. The distillate was separated from the water, shaken twice with fresh water, dried over potassium carbonate and fractionated through a column. The fraction boiling below 90° (mostly 75–80°) was collected as hydrocarbon, and amounted to about 50% of the theoretical yield. The higher boiling fraction distilled over practically entirely between 110–135°, mostly above 125°, and, as will be seen later, consisted of an unsaturated alcohol. The hydrocarbon fraction was refractioned and the

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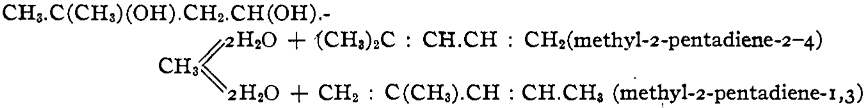
[1] THIS JOURNAL, 31, 722 (1909).

[2] *Ber.*, 34, 2858 (1901).

[3] Elbs and Brand, *Z. Elektrochem.*, 8, 783 (1902); *Chem. Zentr.*, 1912, II, 1756.

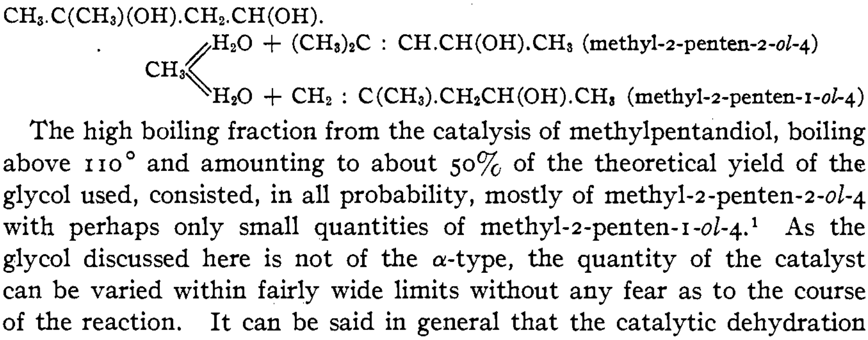
[4] D. R. P. 241,896; *Chem. Zentr.*, 1912, I, 176.

methylpentadiene was found to boil constant at 75.5–76.5°. As there is a possibility for the formation of the isomer, methyl-2-pentadiene-1,3, a small quantity of it may have been present in the hydrocarbon obtained above. This isomer, as will be described later on, boils at 76–77°, hence, the separation of the two hydrocarbons by fractional distillation is not possible. The dehydration of the methylpentandiol would have taken place as follows, with the first equation denoting, very probably, the course of the main reaction:



$$CH_3.C(CH_3)(OH).CH_2.CH(OH).\text{-}CH_3 \begin{cases} 2H_2O + (CH_3)_2C : CH.CH : CH_2 \text{(methyl-2-pentadiene-2–4)} \\ 2H_2O + CH_2 : C(CH_3).CH : CH.CH_3 \text{ (methyl-2-pentadiene-1,3)} \end{cases}$$

That the first is the main reaction is supported by the general observation that there is more tendency for a tertiary hydroxyl to come off with a secondary rather than with a primary hydrogen atom. This is, for example, true of tertiary amyl alcohol, whose dehydration results in the formation of trimethylethylene; while only small quantities of the isomeric methylethylethylene ($CH_2 : C(CH_3).CH_2.CH_3$) are obtained. The reaction with the glycol would then proceed in two steps, the first step being the formation of the unsaturated alcohols as follows:



$$CH_3.C(CH_3)(OH).CH_2.CH(OH).CH_3 \begin{cases} H_2O + (CH_3)_2C : CH.CH(OH).CH_3 \text{ (methyl-2-penten-2-}\mathit{ol}\text{-4)} \\ H_2O + CH_2 : C(CH_3).CH_2CH(OH).CH_3 \text{ (methyl-2-penten-1-}\mathit{ol}\text{-4)} \end{cases}$$

The high boiling fraction from the catalysis of methylpentandiol, boiling above 110° and amounting to about 50% of the theoretical yield of the glycol used, consisted, in all probability, mostly of methyl-2-penten-2-*ol*-4 with perhaps only small quantities of methyl-2-penten-1-*ol*-4.[1] As the glycol discussed here is not of the α-type, the quantity of the catalyst can be varied within fairly wide limits without any fear as to the course of the reaction. It can be said in general that the catalytic dehydration of ditertiary α-glycols is a much more sensitive reaction than that of the secondary-tertiary and disecondary β-glycols.

Glycols containing a primary hydroxyl, such as butandiol-1,3 cannot be dehydrated to the corresponding divinyl hydrocarbon by the methods described in this paper. This is undoubtedly due to the stability of the primary halide. These glycols are dehydrated to some extent giving rise to appreciable quantities of the unsaturated primary alcohols as follows:

$$HCR(OH)CHR.CH_2OH = HCR : CRCH_2OH + H_2O.$$

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[1] There is a possibility for the formation of two other isomeric unsaturated alcohols with a tertiary hydroxyl group. However, as tertiary hydroxyl groups are much more mobile than the secondary, the quantities of these tertiary alcohols would be insignificant even if present. All four isomeric alcohols would give, on dehydration, the two hydrocarbons which are discussed above, and none other.

I have also tried to dehydrate trimethylethylene glycol—$(CH_3)_2C(OH).CH(OH).CH_3$—a tertiary-secondary α-glycol, in a similar manner to isoprene, but the results were of a negative nature.

Polymerization of Methyl-2-pentadiene-2,4.—Several cubic centimeters of the dry hydrocarbon were introduced in a sealing tube and treated with a few pieces of sodium. The air in the tube was displaced by carbon dioxide, the tube was sealed and left in the steam bath. After two days the liquid was found to have solidified. This solid substance was treated according to the directions of Harries,[1] and was found to have rubber-like properties. This fact would be in support of the assumption that the hydrocarbon had conjugated double bonds.

II. Dehydration of a disecondary β-glycol.—The simplest representative of a disecondary β-glycol is pentandiol-2,4-$CH_3CH(OH).CH_2.CH(OH)CH_3$. This substance is very easily obtained by the electrolytic or amalgam reduction of hydracetylacetone, $CH_3.CH(OH).CH_2.CO.CH_3$.

Piperylene-pentadiene-2,4.—Twenty grams pentandiol were treated with about 1 g. hydrobromic acid solution, and decomposed as above described. The reaction was carried out by the addition of fresh glycol, and small amounts of the acid, whenever the reaction was observed to slow down. The catalysis was discontinued when the distillate amounted to about 60 cc. This was separated from the water of dehydration, shaken twice with a little cold water, dried over potassium carbonate and fractioned through a Young's column. Twenty-five cc. of the liquid distilled over below 60°, while the residue amounted to 18 cc. This residue boiled between 115–125°, and consisted evidently of pentene-2-*ol*-4, the partial dehydration product of the glycol. Grignard[2] gives the boiling point of this unsaturated secondary alcohol as 120–122°. The crude hydrocarbon fraction boiling below 60° was refractioned, and the hydrocarbon collected as piperylene boiling at 42.5–45°, mostly 43–43.5°, amounted to 18 g. It is seen that the yield of the hydrocarbon was at least 50%. The yield can probably be increased by a careful study of the conditions of catalysis.

It is evident now that ditertiary, tertiary-secondary and disecondary glycols, with the exception of the α-isomers in the last two cases, can be dehydrated to the corresponding divinyl hydrocarbons by the catalytic action of small quantities of halogen acids or their derivatives, which on dissociation liberate these acids. The mechanism of these reactions may be explained simply by the following equations:

$$(CH_3)_2C(OH).CH_2.CH(OH)CH_3 + HX = (CH_3)_2CX.CH_2CH(OH).CH_3 + H_2O.$$

$$(CH_3)_2CXCH_2CH(OH).CH_3 = (CH_3)_2C : CH.CH(OH)CH_3 + HX.$$

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

[2] *Ann. chim. phys.*, [7] 24, 465 (1901).

This reaction explains the presence of the considerable quantities of the unsaturated alcohols among the decomposition products of the glycols. Part of this unsaturated alcohol is esterified and subsequently dehalogenated to the hydrocarbon. As the water formed in the reaction keeps distilling over with the hydrocarbon and some of the alcohol, it could not play a prominent part in influencing the course of the reaction. The last steps in the dehydration of the glycol may then be represented as follows:

$$(CH_3)C : CH.CH(OH).CH_3 + HX = (CH_3)_2C : CH.CHX.CH_3 + H_2O.$$

$$(CH_3)_2C : CHCHX.CH_3 = (CH_3)_2C : CH.CH : CH_2 + HX.$$

This course of the reaction is supported by the observations of Charon[1] on the reactivity of the hydroxyl of crotonyl alcohol. Charon observed that buten-2-*ol*-1 is very easily esterified by the halogen acids, even in the cold, and that these same acids, contrary to their usual action, did not have any appreciable tendency to add at the double bond. In fact, the reactivity of the hydroxyl group is such that the esterification "is almost immediate, reminding one of the precipitation of a salt" and that the reaction " is much more easy and energetic than in the case of the corresponding saturated compounds." These derivatives of the alcohols are fairly unstable, reminding one of the halogen derivatives of carboxylic acids. "These facts are due to the electronegative character of the molecule, and it must be remarked that this character is much more accentuated for the *propenyl* group—$CH_3.CH : CH$—than for the vinyl group—CH_2:-CH." In crotonyl alcohol the hydroxyl group and the double bond are in the β-position to each other, which is also true of the unsaturated alcohols discussed in this paper, with this difference that the halogen esters formed in the latter case, being derivatives of secondary and tertiary alcohols, would be less stable at the temperature of reaction, and hence they are readily dehalogenated to the corresponding diethylenic hydrocarbons. This reasoning would probably be true in considering the mechanism of the dehydration of ditertiary α-glycols, where the partial dehydration product would be of the type of dimethylisopropenylcarbinol, $(CH_3)_2C(OH).C(CH_3) : CH_2$. In this case, however, because of the molecular structure, part of the alcohol may be metamerized to pinacoline under the influence of the acid reacting catalyst. That dimethylisopropenyl carbinol would be dehydrated to the hydrocarbon is made evident by the observation of Mariutza,[2] who obtained the hydrocarbon by heating the alcohol on the water bath with very dilute hydrochloric acid (0.1%). It would be interesting to know if Mariutza obtained any pinacoline in this reaction, as there is no mention made of the formation of other definite substances.

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[1] *Compt. rend.*, **128**, 736 (1899).

[2] *J. Chem. Soc.*, **58**, 728 (1890).

Part III. Dehydration of Unsaturated Alcohols.

Methyl-2-pentadiene-2,4.—The unsaturated alcohol used in this reaction was that obtained by the partial dehydration of methyl-2-pentadiol-2,4. It has been noted above that the catalysis of this glycol results in the formation of approximately equal quantities of the hydrocarbon and the alcohol. The boiling point of this alcohol, $(CH_3)_2C : CH.CH(OH).CH_3$, was found to be 130°. It is not necessary to purify the alcohol in case it is obtained from the glycol. The residue from the hydrocarbon, boiling above 110°, is dehydrated directly in the usual form of apparatus described above. Twenty-five grams of methylpentenol are treated with about 0.5–1 g. hydrobromic acid solution (aniline hydrobromide can be used with very good results) and the decomposition carried out at such a rate that the vapors distil over below 95°. Fresh alcohol is dropped in and the reaction continued as long as desired with the addition of small amounts of the catalyst in case the reaction slows down. The distillate is treated as under the glycol and the hydrocarbon purified by fractional distillation. The higher boiling fractions containing unchanged alcohol are catalyzed again. By repeating this process it is possible to decompose the unsaturated alcohol almost quantitatively to the hydrocarbon. As the alcohol was obtained from methyl-2-pentandiol-2,4, it follows that the dehydration of the glycol can be made nearly quantitative. I would mention here, that the hydrocarbon (see under the glycol) was polymerized by Harries' sodium process to a rubber-like substance.

Methyl-2-pentadiene-1,3, $CH_2 : C(CH_3).CH : CH.CH_3$.[1]—This hydrocarbon was mentioned in the discussion of the catalytic dehydration of methyl-2-pentandiol-2,4. It was observed that this isomer of methyl-2-pentadiene-2,4 might have been formed in small quantities in the decomposition of the glycol. The unsaturated tertiary alcohol used in this experiment was obtained, as noted in a previous paper, by the interaction of methylmagnesiumiodide and ethylideneacetone. The catalysis was carried out as usual using 0.2–0.4 g. of aniline hydrobromide in dehydrating 40 g. of the alcohol. This amount of the salt would have been sufficient to decompose much greater quantities of the alcohol, had it been necessary to do so. The reaction in this case, as in the last, was extremely easy and smooth. The distillation of the decomposition products took place below 85°. The distillate was treated as usual, and fractioned through a column. 70% of the liquid distilled over below 85°, mostly at 76–79°. This was

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[1] Harries (*Ber.*, **34**, 301–302) reports that he obtained this hydrocarbon by heating the phosphate of $(CH_3)_2C(NH_2).CH_2.CH(CH_3)NH_2$. He gives its b. p. as 75–77°. As the diamino compound is a derivative of methyl-2-pentandiol-2,4, if the discussion of the mechanism of the dehydration of the glycol holds true in the case of the diamino compound, the hydrocarbon of Harries must have been of the same nature as that obtained from the glycol, and must have consisted to a greater extent of methyl-2-pentadiene-2,4.

refractioned and the hydrocarbon was found to boil at 76–77°. The residue, about 30%, was found to consist of the unchanged alcohol, and was dehydrated again. The total residue from this reaction that resisted dehydration did not amount to more than 1 g., and was found to consist of methylisobutylketone, which had been formed in the preparation of the alcohol in the Barbier-Grignard reaction.[1] The dehydration of the alcohol took place, most probably, according to the following equations:

$$CH_3.CH : CH.C(CH_3)_2(OH) + HX = CH_3.CH : CH.C(CH_3)_2X + H_2O.$$

$$CH_3.CH : CH.C(CH_3)_2X = CH_3.CH : CH.C(CH_3) : CH_2 + HX.$$

Gry[2] states that the hydrocarbon obtained by him from the same alcohol by the action of acetic anhydride or acetylchloride, and boiling at 76–79°, "precipitates mercuric chloride in an aqueous solution, it is therefore probably, an allene, and must consequently possess the formula CH_3-$CH : C : C(CH_3)_2$; it would be therefore identical with trimethylallene of Ipatieff." Ipatieff[3] obtains the latter hydrocarbon, as is usual with such compounds, by the dehalogenation of methyl-2-bromo-3-penten-2, by heating this substance with alcoholic potassium hydroxide at 150°. The reaction took place as follows: $(CH_3)_2C : CBr.CH.CH_3 - HBr = (CH_3)_2C : C : CH.CH_3$.

In every instance where the dehydration of *unsaturated alcohols* to diolefines has been studied, it has been observed that the hydrocarbons contain conjugated double bonds. I do not know of a single case where it has been conclusively proven that the hydrocarbon obtained was not of the butadiene-1,3 type. The fact that a number of hydrocarbons obtained from the glycols and the alcohols mentioned in this paper were capable of polymerization to rubber-like masses, together with the observations of Reif,[4] Abelmann,[5] etc., force me to believe that the hydrocarbon obtained in this experiment also was none other than the divinyl derivative.

Isoprene.—About 10 g. methyl-3-buten-1-*ol*-3, $(CH_3)_2C(OH).CH : CH_2$, were treated with about 0.5 g. aniline hydrobromide, and the decomposition carried out as usual. Fifteen grams more of the alcohol were gradually dropped in, and the reaction continued until finally about 3 cc. of a liquid were left in the reaction flask. This liquid consisted mostly of the water of dehydration; while the insoluble organic layer was less than 1 cc. The catalysis was very smooth, and the reaction products distilled over below 80°. This reaction does not seem to induce any appreciable dimerization of the hydrocarbon, as is the case when the alcohol is treated with the

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[1] See my paper on "Barbier-Grignard reactions."

[2] *Bull. soc. chim.*, [4] **3**, 379 (1908).

[3] *J. prakt. Chem.*, **59**, 535 (1899).

[4] *Ber.*, **41**, 2739 (1908).

[5] *Ibid.*, **43**, 1574 (1910).

usual "dehydrating" acids, such as oxalic and phosphoric acids. The decomposition products were dried over potassium carbonate and submitted to fractionation. Half of the liquid boiled constant at 35.5°, while the rest distilled over mostly at 97°, leaving practically no residue boiling above 100°. It is evident, therefore, that this high boiling fraction consisted of the unchanged isoprene alcohol, which was used over again. The side products are very little in amount, and may be due to impurities in the methylbutenol used. The fact that the hydrocarbon boiled constant at 35.5° is evidence of the purity of the isoprene.

Sodium isoprene rubber.—The hydrocarbon obtained as isoprene was treated in a small bottle with a few pieces of sodium, and left at room temperatures in diffused light, after stoppering well the bottle. The hydrocarbon soon began to show signs of thickening and contraction, and within one week was found to have solidified. The bottle was then heated at 60° for several hours, and its contents were immediately afterwards treated according to the directions of Harries.[1] We thus obtained a good yield of a tough and elastic rubber-like substance.

As both tertiary and secondary unsaturated alcohols are catalyzed to the corresponding diethylenic hydrocarbons, it is to be assumed that even methyl isopropenyl carbinol, treated as above with small quantities of a catalyst, will be decomposed to isoprene as follows:

$$CH_2 : C(CH_3).CH(OH).CH_3 + HX = CH_2 : C(CH_3).CHX.CH_3 + H_2O.$$

$$CH_2 : C(CH_3).CHX.CH_3 = CH_2 : C(CH_3).CH : CH_2 + HX.$$

There is a German patent,[2] assigned to the Elberfelder Farbenfabriken, which deals with the preparation of isoprene from methylisopropenyl carbinol. The reaction is carried out by treating the carbinol "with *dehydrating agents*, such as potassium bisulfate, mineral acids, zinc chloride, anhydrous oxalic acid, etc." The examples given comprize heating the alcohol with oxalic acid, distilling it over potassium bisulfate, and treating it in the cold with phosphorus pentachloride. It is known[3] that these methods seldom give very good results. In every case there is more or less di- and poly-merization of the hydrocarbon formed.

The processes described in this paper are entirely new, never used before in the dehydration of glycols or unsaturated alcohols to butadiene-1,3 hydrocarbons. The only cases that might be taken as somewhat similar are two: the first case relates to the dehydration by Mariutza[4] of dimethylisopropenylcarbinol, a tertiary alcohol, which was carried out by boiling the carbinol with very dilute aqueous hydrochloric acid (0.1%). The

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

[2] Ditmar, "Die Synthese des Kautschuks," p. 70; *J. Soc. Chem. Ind.*, 30, 1230 (1911); *C. A.*, 6, 2554 (1912).

[3] Reif. *Ber.*, 41, 2743; Abelmann, *Ibid.*, 43, 1577.

[4] *J. Chem. Soc.*, 58, 728 (1890).

second case is that reported by Abelmann,[1] who observes that in attempting to esterify the unsaturated alcohols, obtained by the interaction of tiglic aldehyde and organomagnesium compounds, by Norris's[2] method using hydrobromic acid, he obtained the hydrocarbon instead. The esterification method of Norris consists in heating one part of the alcohol with 2–3 parts of the equivalent amount of a constant boiling mixture of hydrobromic acid and water. This means that the reaction being carried out in presence of a large excess of the acid, the hydrocarbons obtained by Abelmann will be partly acted upon by the acid to give rise to brominated derivatives. In fact, although Abelmann obtained a fair yield of the divinyl hydrocarbon, he states "the drawback of this method consists in that the hydrocarbon is made impure to a greater or less degree by bromides or even bromine, the complete elimination of which offers certain difficulties." From the final yield of the purified hydrocarbon which he obtains (60%), it is easy to see that the process of Abelmann is far from being ideal. By means of the processes I have described in this paper it is possible to obtain a very pure hydrocarbon by a simple fractionation. The by-products consist practically entirely of the unsaturated alcohols, which can be dehydrated likewise to the hydrocarbon, so that the final yield of the hydrocarbon, in most cases, approximates the theoretical. The amount of catalyst used is in most cases insignificant as compared with the quantity of substance dehydrated. The method described above is not operative in the case of unsaturated primary alcohols, which behavior is due to the fact that the primary esters are stable at the temperatures of reaction.

Part IV. Dehydration of Saturated Tertiary Alcohols.

Although this chapter, properly speaking, does not come under the heading of *butadiene-1,3 hydrocarbons*, I take the liberty to insert it here, because of the similarity in the processes used. The success in dehydrating glycols and unsaturated alcohols, led me to consider the possibility of a similar catalysis of saturated alcohols in the wet way. Tertiary alcohols are distinguished from the primary and secondary alcohols by the comparatively greater reactivity of their hydroxyl group. Among the known methods[3] for the generation of olefines by the direct dehydration of alcohols in the wet way, we have the reactions which consist in heating the alcohols with dehydrating agents, such as sulfuric, phosphoric and oxalic acids, zinc chloride, etc. Tertiary alcohols are known to suffer dehydration in many esterification processes. Thus, when dimethylisopropyl carbinol, $(CH_3)_2C(OH)CH(CH_3)_2$, is made to react with acetic anhydride in presence of a few drops of concentrated sulfuric acid or a little zinc chloride,

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[1] *Ber.*, 43, 1577–1578, 1587 (1910).

[2] *Am. Chem. J.*, 38, 632 (1907).

[3] "Lehrbuch," Meyer-Jacobson, 2nd ed., part I, pp. 816, 817, 819.

it is dehydrated to a mixture of unsaturated hydrocarbons, tetramethylethylene, and methylisopropylethylene. Tertiary amyl alcohol[1] is also easily dehydrated to the olefine by the action of a solid organic acid and phosphoric acid. The best method known is that of heating the tertiary carbinol at 60–70° with oxalic acid. The hydrocarbon obtained in this way is said to be pure trimethylethylene. Kondakoff,[2] on the other hand, states that the hydrocarbon obtained by the dehydration of tertiary amyl alcohol, always contains some of the isomeric methylethylethylene, $CH_2 : C(CH_3).CH_2.CH_3$. Wolkoff[3] in a report on the action of acids and their esters on alcohols at high temperatures, refers to the unfinished work of Bugajeff, in which the latter observed that very small amounts of any acid or ester induced the dehydration of secondary butyl alcohol to β-butylene. Wolkoff, on the basis of Bugajeff's observation, undertook the systematic study of the alcohols and discovered that secondary alcohols when heated in sealed tubes to above 200°, either alone or in presence of small amounts of acetic acid and its derivatives, did not suffer any change. On the other hand, if secondary and tertiary alcohols were heated to a little above 200° in presence of traces of a halogen acid or a halogen ester, they were decomposed completely to the corresponding hydrocarbon and water. Hydriodic acid and methyliodide were found to be the best agents to effect this dehydration. Tertiary alcohols naturally reacted more violently than secondary alcohols. Primary alcohols when heated with methyliodide were etherified.

The action of halogen acids on alcohols at their boiling point is that of esterification. Norris,[4] in the paper previously alluded to, observes that, when tertiary butyl alcohol is made to react with concentrated hydrochloric acid in the cold, the chloro ester is formed in quantitative yield. The corresponding bromo- and iodoesters are obtained if the tertiary alcohol is heated with an excess of the constant boiling mixtures of the hydrobromic and hydriodic acids with water. As far as is known to me, there is no indication in the literature that tertiary alcohols can be dehydrated by the action of halogen acids or their derivatives at temperatures below 200°. According to my discovery, saturated tertiary alcohols can be dehydrated similarly to the glycols and unsaturated alcohols.

Trimethylethylene, $(CH_3)_2C : CH.CH_3$. *Experiment I.*—The apparatus used was similar to the one described in Experiment I of Part I. Fifty grams of dimethylethylcarbinol were treated with about 3 cc. hydriodic acid solution, boiling at 125°, and the mixture heated over a wire gauze. The decomposition products distilling through the column showed at

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[1] *Ber.*, 26, Ref. 342 (1893).

[2] *J. prakt. Chem.*, **54**, 454 (1896).

[3] *Chem. Zentr.*, 1890, II, 41.

[4] *Am. Chem. J.*, 38, 631, 632 (1907).

first a temperature of about 50°, which was evidently due to the fact that the distilling products consisted mostly of the hydrocarbon. As the accumulation of the water of dehydration progressed, the temperature of the vapors increased and water and some alcohol began to come over. The highest temperature registered by the vapors was 80°. The reaction was continued by dropping in fresh alcohol. The distillate was separated from the water, dried over potassium carbonate, and fractioned through a column. The fraction boiling below 50°, and amounting to over 50% of the dried product, was refractioned, and the liquid boiling at 36–40° was collected as trimethylethylene. The higher boiling fractions consisted entirely of the unchanged tertiary alcohol and could be used over again. The dehydration of dimethylethylcarbinol can therefore be made quantitative by this process. The only products left in the flask consist of traces of iodide which can be used to catalyze more of the alcohol.

Experiment II.—Fifty grams of the carbinol were treated with 4 g. aniline hydrobromide and 2 cc. of a concentrated solution of hydrobromic acid. The reaction was carried out as in the last experiment, and the highest temperature registered by the vapors of the decomposition products was 75°. Fresh alcohol was dropped into the flask and the catalysis continued for quite a long time. The pure hydrocarbon obtained amounted to about 50%, while the rest of the products consisted of unchanged alcohol. The reaction in both experiments was very smooth and regular, and it is in my opinion the best process for preparing the hydrocarbon. Other tertiary alcohols, and *possibly* secondary alcohols having a high boiling point, would react similarly. The hydrocarbon obtained in the last two experiments is undoubtedly trimethylethylene, containing, very probably, small quantities of the isomeric methylethylethylene, as noted by Kondakoff.[1] The reaction may be said to have proceeded as follows:

$$(CH_3)_2C(OH).CH_2.CH_3 + HX = (CH_3)_2CX.CH_2.CH_3 + H_2O$$

$$(CH_3)_2CX.CH_2CH_3 = (CH_3)_2C : CH.CH_3 + HX$$

$$[(CH_3)_2CX.CH_2.CH_3 = CH_2 : C(CH_3).CH_2.CH_3 + HX]$$

Discussion of Results.

In this and the preceding two papers, I have reported on some new processes for the preparation of butadiene-1,3 hydrocarbons.[2] Among these, those discussed in this paper are by far the simplest. Whereas in the pyrogenetic catalyses the yields of the hydrocarbons may be made to approximate the theoretical, still the processes are quite complicated. The tendency of the butadiene hydrocarbons to decompose at the high temperatures of reaction would necessitate the use of vacuum, which

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[1] *J. prakt. Chem.*, **54**, 454 (1896).

[2] It is very probable that hydrocarbons containing more than two conjugated double bonds can be prepared from *similarly constituted* hydroxyl compounds, having already in the molecule one or more double bonds.

would complicate the process still further. In this latter instance, it would be necessary to use refrigerating agents or other mechanical devices for avoiding the loss of valuable hydrocarbon. If, on the other hand, the pyrogenetic decomposition is carried out at ordinary pressures, the hydrocarbons will have to be purified by chemical means. The catalytic methods in the wet way can be carried out in the simplest form of apparatus, with practically no loss of hydrocarbon, with the further advantage that the latter can be freed from the accompanying *only* impurity—the unsaturated alcohol—by fractional distillation. Furthermore, the quantity of catalyst used is, as a rule, so small in comparison with the amount of substance catalyzed, that these catalyses in the wet way may be spoken of as being ideal from every point of view. There is one point, however, in which the pyrogenetic methods are superior to the wet methods, and that consists in the more general nature of the former. The oxides, secondary-tertiary and disecondary α-glycols, glycols having a primary hydroxyl group, as well as unsaturated primary alcohols cannot be catalyzed to the corresponding butadiene-1,3 hydrocarbons in the wet way. The decomposition of these substances, as already described, can be successfully carried out by the pyrogenetic catalytic methods.

The preparation of the hydrocarbons directly from the hydroxyl compounds is the simplest of all known methods. The use of the quaternary ammonium derivatives, the chlorhydrins, or the dihalogen substitution products of these hydroxy-compounds, the unsaturated halides, etc., complicate the processes needlessly. I believe that I have indicated the lines along which work will be done in the future for the *commercial* preparation of the hydrocarbons in the synthesis of "rubber." This problem will eventually be solved, although it will require a good many years of earnest and patient study. The starting point in these syntheses will most probably be alcohol, which can be produced fairly cheaply.

Before concluding my reports on the work we have carried out in the synthesis of the divinyl hydrocarbons, I would like to state that we have left much that we would have liked to have finished. We would have liked, for example, to have made analyses of every compound obtained, prepared the halogen derivatives of the hydrocarbons for a better characterization of them; and above all, we would have liked to have studied the chemical and physical properties of the different isomeric hydrocarbons. Being outside of a truly scientific institution, and being moreover driven by the desire to save something out of the mad rush for patenting every conceivable and inconceivable organic reaction in the synthesis of these hydrocarbons, such as is still going on, we had very little time left at our disposal for anything else.

And now, that fortune has decreed that I should relinquish, at least for the present, this most fascinating of organic investigations, I would state that I have tried to derive the most rational conclusions possible under the circumstances from the experiments described in this and the previous papers, and that I shall be ever ready to acknowledge any false conclusions I may have arrived at. The processes described by me have simplified the problem of the preparation of the unsaturated hydrocarbons, and I hope that they will be made use of in the systematic study of this branch of organic chemistry which is still in a more or less chaotic[1] state.

In conclusion, I would like to express my indebtedness to my colleague, R. B. Earle, for many valuable suggestions, and to thank him again for his constant help in carrying out a good many of the experiments described in this and the previous papers.

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THE PREPARATION OF ALLYL IODIDE.

BY RASIK LAL DATTA.

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The preparation of large quantities of allyl amine for conversion into the nitrite, necessitated the preparation of still greater quantities of allyl iodide, since allyl amine was obtained from this through the isothiocyanate. The method used for the preparation of allyl iodide was the action of yellow phosphorus on iodine in glycerol. This method is attended with some difficulty, and hence it has engaged the attention of chemists who have published modifications of the method from time to time. On undertaking the preparation of the compound, the various methods were tried, but it was found that in no case had the real difficulties been overcome. After a series of careful experiments, a modified method was devised, in which, as will be shown later, the difficulties were reduced to a minimum, and by which the preparation could be completed smoothly and in a very short time. Behal[2] in order to obviate the use of yellow phosphorus, employed red phosphorus in conjunction with a solution of iodine in allyl iodide and glycerol. This method does not, however, come under our consideration.

Claus[3] described the preparation of this compound in detail for the first time. His results were confirmed by James.[4] Claus did not use carbonic acid gas in this method. The yield obtained was 220 g. of pure allyl iodide from 240 g. of iodine.

Later, Kanonikoff and Saytzeff published a modification of the method

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[1] This is especially the case with the higher members of the unsaturated hydrocarbon series, where the possibility for the formation of a number of isomers, and their presence in the products obtained in the reactions, make their identification quite difficult and highly desirable.

[2] *Bull. soc. chim.*, **47**, 876 (1887).

[3] *Ann.*, **131**, 58 (1864).

[4] *Ibid.*, **185**, 191 (1877).