added last. Where a blue color was formed it generally developed immediately, before the formation of any precipitate. The colors produced in some cases were extremely intense and very permanent. As stated above 4,5-diaminouracil gives no color with the uric acid reagent in acid solution. When the test is applied according to the above conditions, in the presence of ammonia, an intense blue color is produced.

An examination of Table I will reveal the interesting fact that the 5-amino group is apparently the functionating group when phosphotungstic acid (uric acid reagent) produces a blue color in an ammoniacal solution. In every case examined by us the presence of an amino or imino group in the 5-position of the ring was necessary in order to obtain a blue color by use of the uric acid reagent. If both hydrogens were replaced by other groups or the 5-amino group placed in any other position in the ring or substituted in some side chain this reagent always failed to give a color in alkaline solution. It is interesting to note at this time that alloxantine also gives a blue color with the uric acid reagent in an ammoniacal solution. Whether other 5-hydroxypyrimidines behave in a similar manner will be determined by further work. 5-Hydroxypyrimidines possess many properties in common with the aromatic phenols.

NEW HAVEN, CONN.

NEW PROCESSES FOR THE PREPARATION OF BUTADIENE-1,3 HYDROCARBONS. II. PYROGENETIC DECOMPOSITION OF HYDROXY-COMPOUNDS.

BY L. P. KYRIAKIDES.

Part I. Catalytic Dehydration of Glycols.

In the first paper on these processes, it was shown that methyl-2-butylene-oxide-1,2 could be easily and smoothly dehydrated to isoprene. As oxides are anhydrides of the glycols, it occurred to me that the latter substances also might be made to give hydrocarbons of the butadiene-1,3 series. In the literature on the subject of dihydroxyl compounds, we read that α-glycols are easily transformed to aldehydes or ketones, after partial dehydration. This transformation is effected most readily by heating the glycols with dehydrating agents or dilute acids. The reactions[1] are explained on the assumption that the dehydration of the glycols results in the formation of either the corresponding oxide, or the homologue of vinyl alcohol. It is known that oxides are metamerized to aldehydes or ketones by the action of acid substances or high temperatures; while alcohols of the *vinyl* series, being incapable of existence in the free state, are metamerized to the carbonyl substances at the moment of their formation. Among the α-glycols, those containing two tertiary hydroxyl groups, the

[1] Lehrbuch der org. Chemie, Meyer-Jacobson, 2nd ed., Vol. I, Part I, pp. 648–649.

pinacones, are especially susceptible to such reactions. Pinacones are easily made to lose one molecule of water and then to give rise to ketones. This takes place by a molecular rearrangement, due to the wandering of an alkyl group. In the case of these ditertiary α-glycols, it has been observed that they can be made to lose two molecules of water and give rise to hydrocarbons with conjugated double bonds. This dehydration[1] is best carried out by distilling pinacone over alumina at 400°.

β-Glycols were studied by Lieben and his co-workers. If butandiol-1,3[2] is heated with dilute sulfuric acid, it is decomposed to a number of substances, among which n-butyraldehyde and methylethylketone are easily detected. That β-glycols, also, are mainly decomposed to substances containing the carbonyl group is further proven by the observations of Kadiera,[3] who obtained only butyraldehyde and methylethylketone by treating butandiol-1,3 with 50% sulfuric acid in the cold. Lieben[4] observes that the nature of the products obtained by the action of dehydrating agents, dilute acids or of water at high temperatures on β-glycols, depends on the constitution of the glycol. The main products are, then, aldehydes, ketones or 1,4-oxides. I began the study of the catalytic dehydration of the dihydroxyl compounds with the 1,3-glycols, which are, as a rule, more readily obtained than the α-isomers.

Butadiene-1,3 (Divinyl), $CH_2 : CH.CH : CH_2$.—*Divinyl* is the simplest representative of the hydrocarbons containing conjugated double bonds, and is capable of polymerization to a rubber-like mass. Harries,[5] who studied the hydrocarbon and its polymerization products, observes that the sodium butadiene rubber was vulcanized to a product that surpassed the other synthetic rubber-like substances in elasticity and strength. The handling of divinyl, which is a gas at ordinary temperatures, is not very easy. Our experience with this hydrocarbon was not very enjoyable, as in the majority of cases the sealed tubes exploded during the heating. The glycol used in the following experiments was obtained by the reduction of acetaldol.

Experiment I.[6]—95 g. β-butylene glycol were slowly dropped into a tube filled with pieces of ignited kaolin. The dehydration was effected at 380–400°, and the decomposition products were collected in a receiver cooled with a mixture of carbon dioxide and ether. The gaseous decomposition products were dried by passing them through a drying tower containing calcium chloride, and then condensed in a sealing tube. The

[1] D. R. P. 235,311, *Chem. Zentr.*, 1911, II, 112; Fr. Pat. 417,275, *C. A.*, 6, 2548 (1912).

[2] Bauer, *Monatsh.*, 25, 1 (1904).

[3] *Monatsh.*, 25, 340.

[4] *Ibid.*, 23, 74 (1902).

[5] *Ann.*, 383, 206, 213; 395, 241, 259.

[6] This experiment was carried out on the 14th day of Dec., 1911.

amount of liquid condensed measured about 8 cc. This was treated with a little catalyst favoring normal polymerization, and submitted to the action of heat after sealing the tube. The latter was left in a steam bath for 72 hours, when the liquid was found to have thickened appreciably. In order to increase the rate of polymerization, the tube was heated in a bomb furnace at 120° for 72 hours more, and the hydrocarbon was thus made to solidify. On opening the tube we observed quite a little pressure, which was due to unpolymerized divinyl or other gaseous impurities. The solid product was submitted to steam distillation and was found to be a tough and elastic sample of a rubber-like substance. This substance, on being left in the air for a short time, is soon changed in its physical properties, becoming very hard and brittle. This is evidently the result of chemical changes due to oxidation.

Senderens,[1] in a review on the dehydration of saturated alcohols, remarks that the temperature and rate of catalysis are functions of the physical as well as chemical nature of the catalyst. Having studied the activity of a good many catalysts, Senderens concludes that carefully prepared and ignited aluminum oxide is the best catalyst; but the disadvantage in its use is that this substance is very sensitive towards impurities and heat. Kaolin and aluminum silicate are spoken of as being very active. Impurities and heat do not effect an appreciable decrease in the activity of these substances.

As we had on hand a sample of commercial aluminum phosphate, which was marked as *chemically pure*, we made use of it in the following experiment. Senderens speaks of aluminum phosphate as being only a fair dehydrating agent.

Experiment II.—75 g. of the glycol were catalyzed over ignited aluminum phosphate at 450° and 150 mm. The distillation of the liquid was carried out slowly, and the gases were condensed as in the last experiment. The water formed as a result of the reaction measured 28 cc.—the theoretical amount is 30 cc. The organic layer had a very clean appearance, was very light yellow in color and measured about 50 cc. The gaseous products were partially purified by passing them through two bulbs containing concentrated potassium hydroxide, and then dried by means of calcium chloride. The alkaline liquids, contained in the bulbs, gradually deepened in color as the distillation of the gases progressed, and finally were covered with a little layer of a resinous substance. As the distillation of the dehydration products was finished by warming the receiver with the hand, any acetaldehyde present would be carried over into the alkaline solution, where it would be resinified. The production of acetaldehyde is probably due to the decomposition of any unreduced acetaldol present in the glycol. The divinyl as purified above was condensed in three tubes. The first

¹ *Ann. chim. phys.*, [8] 25, 449 (1912).

tube, containing about 5 g. of the hydrocarbon and a few pieces of sodium, was sealed and heated at 60° for about 30 hours. The liquid was found to have solidified completely at the end of this period of heating. The contents of the tube were treated according to the directions of Harries, and the rubber was found to be fairly tough. The other two tubes, containing the hydrocarbon and a little of a catalyst, were sealed and heated one week at 100° and another at 110°. The liquid in one of the tubes was solid. The other tube, with the hydrocarbon still showing signs of mobility was heated for 15 hours more at 120°. The crude polymerization products were subjected to steam distillation and then dried. The substance obtained thus had the physical properties of crude rubber. It is seen that butadiene is more readily polymerized to a rubber-like substance than isoprene. In cases where the sample of divinyl was very impure, we could usually obtain a solid mass, no matter how small, on heating it for a week or two at 100–110°.

The fact that the gases obtained by the pyrogenetic dehydration of butandiol-1,3 were capable of polymerization to rubber is ample proof of the formation of divinyl. In some catalyses the products of decomposition, especially those obtained in partial vacua (below 50 mm.) and at temperatures varying between 420–460°, were very clean in appearance and contained very little high boiling side-products. The low boiling products would easily solidify to rubber-like masses. A sample of such a decomposition product of β-butylene glycol was submitted to normal polymerization by heating in the steam bath. The liquid showed signs of rubber formation within 24 hours. The tube having exploded on the third day, we were able to recover about 5 g. of the divinyl as a very fair sample of rubber. The dehydration of the glycol had been effected by aluminum phosphate. Further evidence of the formation of considerable quantities of divinyl, even at ordinary pressures from β-butylene glycol, is found in the fact that on treating the decomposition products with bromine we were able to obtain great quantities of tetrabrombutane. This tetrabromide was dehalogenated according to Gustavson and Demjanoff's[1] zinc dust method, and the hydrocarbon polymerized to rubber. The choice of a good and active dehydrating agent in these catalyses is very essential. The dehydration of 1,3-glycols to hydrocarbons of the divinyl series, would seem to proceed according to the following course:

(1) $CH_3.CH(OH).CH_2.CH_2OH = CH_3.CH : CH.CH_2OH + H_2O.$
(2) $CH_3.CH : CH.CH_2OH = CH_2 : CH.CH : CH_2 + H_2O.$

R. B. Earle has been able to isolate crotonyl alcohol, $CH_3CH : CHCH_2OH$, among the decomposition products in the formation of divinyl. In fact, β-butylene glycol, if submitted to the action of catalysts at temperatures not exceeding 350°, seems to be dehydrated principally to bu-

[1] *Chem. Zentr.*, **1888**, 1345; also Thiele, *Ann.*, **308**, 339.

tenol. The assumption that crotonyl alcohol is an intermediate step in the complete dehydration of the glycol is supported by the discovery that buten-2-*ol*-1 itself, is readily dehydrated to butadiene-1,3, if subjected to the pyrogenetic action of catalysts. Charon,[1] furthermore, states that, by heating the bromo-ester of the unsaturated alcohol with potassium formate at 160–180°, he obtained the *diene* as the principal product of the reaction. The dehalogenation of bromo-1-butene-2 to divinyl is explained by Charon on the assumption that methylallene, $CH_3.CH : C : CH_2$, is the primary reduction product. This substance, however, is immediately isomerized to the more symmetrically constituted divinyl under the influence of the high temperature, the symmetrical configurations being the stablest of all.

Isoprene, $CH_2 : C(CH_3).CH : CH_2$.—Methyl-2-butandiol-1,3, $CH_3.CH-(OH).CH(CH_3).CH_2OH$, was obtained by the reduction of methyl-2-butanon-3-*ol*-1. Forty g. of the glycol were distilled slowly over aluminum phosphate at 450° and 15–20 mm. The decomposition products were condensed by means of carbon dioxide and ether. The products were separated from the water, dried and fractioned through a column. Ten g. of the liquid boiled at 30–40°. This was refractioned and 5 g. of the substance were obtained by boiling at 34–38°. The low yield of isoprene is explained on the assumption that the rate of catalysis was rather fast. The remarks as to the purity of the hydrocarbon, found in the last paper, would hold true here also. For a very pure sample of isoprene a higher vacuum, than the one used here, must be utilized.

Piperylene, $CH_3.CH : CH.CH : CH_2$.—The pentandiol, $2,4-CH_3.CH-(OH).CH_2.CH(OH).CH_3$, was prepared by the reduction of hydracetylacetone, $CH_3CH(OH)CH_2COCH_3$. Forty grams of the glycol were dehydrated at about 35 mm. as the isoprene above. The water formed as the result of the decomposition amounted to 12 cc.; theory calls for 14 cc. The dried organic liquid was fractioned through a column. A little liquid distilled over below 35°, and had the sharp smell of ethanal, which was probably due to the decomposition of unreduced hydracetylacetone present in the glycol. The fraction collected as piperylene boiled mostly at 40–45° and weighed more than 10 g.

I would like to mention here a reaction, which I did not have the time to study well, but which may, nevertheless, prove to be of considerable importance. It has been known for some time that finely divided copper,[2] made by the reduction of the oxide, has a catalytic action on alcohols at about 300°. Primary and secondary alcohols are thus dehydrogenated to aldehydes and ketones respectively; while tertiary alcohols[3] are dehydrated

[1] *Ann. chim. phys.*, [7] **17**, 234.

[2] Sabatier and Senderens, *Bull. soc. chim.*, [3] **33**, XVII, 263 (1905).

[3] *Ibid.*, also Neave, *The Analyst*, **34**, 346 (1909).

to olefines. On the basis of this last reaction, it seemed to me that a ditertiary α-glycol, such as pinacone, might be dehydrated so as to give rise to a homologue of divinyl. At 300° freshly reduced copper does not catalyze pinacone to a hydrocarbon. The pinacone used was obtained by distilling pinacone hydrate through a column until the temperature of the vapors attained 115°, and the residue from this distillation was made use of in the following experiments.

Dimethyl-2,3-butadiene-1,3, $CH_2 : C(CH_3).C(CH_3) : CH_2$. — Thirty grams of the glycol were slowly distilled over finely divided copper at 430°. The distillate was freed from the water, dried over calcium chloride and fractioned through a column. Five grams of the liquid distilled over below 85°, mostly 70–75°. This liquid had the boiling point of dimethyl-2,3-butadiene-1,3 and the characteristics of an unsaturated hydrocarbon. The substance was dissolved in ether, cooled and treated slowly with bromine. The halogen was absorbed instantly. The addition of bromine was discontinued when the rate of its absorption slowed down appreciably. The solvent was then evaporated off, and the residue left in the ice-chest. We soon observed the deposition of a crystalline substance, which was very probably the tetrabromide of the hydrocarbon. The high boiling fraction from the distillation of the hydrocarbon contained pinacoline. Pinacoline itself, passed over freshly reduced copper at 450–480°, does not undergo any appreciable change. Another experiment was carried out with 40 g. pinacone. The temperature of reaction was kept at 460–500° and the pressure was that obtained by the May-Nelson vacuum pump. The decomposition products were collected at ordinary pressures at the exit end of the pump. The distillate was dried and fractioned through a Young's column, when 5 g. of the liquid distilled over below 90°. This substance was refractioned, and the liquid, boiling at 70° and amounting to 3 g., was brominated as above. In this case also, some of the crystalline tetrabromide was obtained. It seems evident that ditertiary α-glycols can be dehydrated to hydrocarbons of the butadiene-1,3 series, if they are distilled over freshly reduced copper at temperatures above 400°. The dehydration of these glycols could result, normally, only in the formation of pinacolines or hydrocarbons, which can be easily separated by fractional distillation. In the case of pinacone it may be possible to effect a better dehydration to the hydrocarbon by raising the temperature of reaction and carrying it out in vacuo. Methyl-2-buten-3-ol-2, a tertiary unsaturated alcohol, might react in a similar manner to give isoprene as follows:
$$CH_3.C(CH_3)(OH).CH : CH_2 = CH_2 : C(CH_3).CH : CH_2 + H_2O.$$

Part II. Dehydration of Unsaturated Alcohols.

The dehydration of unsaturated alcohols, especially those containing a secondary and tertiary hydroxyl group, is usually effected by means of oxalic acid, potassium acid sulfate or acetic anhydride in the *wet* way.

Reif,[1] who studied the generation of divinyl hydrocarbons from alcohols of the buten-2-ol-1 type with a secondary hydroxyl group, states that he could not obtain the *dienes* by the dehalogenation of the chloro-esters of the alcohols, neither could he dehydrate these alcohols with acetic anhydride. Reif succeeded in dehydrating the unsaturated alcohols directly with potassium acid sulfate; but as this salt induces the partial polymerization of the hydrocarbons during the reaction, he effected the dehydration by using small quantities of the alcohols. In spite of this precaution, he could not obtain yields of the hydrocarbons higher than 15%. Abelmann,[2] on the other hand, discussing the dehydration of unsaturated alcohols, obtained by the interaction of tiglic aldehyde and organomagnesium compounds, has observed that the best way for producing the *dienes* is by dehalogenating the chloro-esters of the alcohols by means of quinoline. In some cases even potassium acid sulfate gave good results. Another method, which Abelmann discusses in the same paper is that of the action of hydrobromic acid in the use of Norris' esterification process. It has been mentioned above that unsaturated alcohols could also be changed to the butadiene-1,3 derivatives by distilling them over heated catalysts, preferably at reduced pressures. This method would be the simplest in many instances, as the yields of the hydrocarbons are very good.

Divinyl.—This is very easily obtained by carrying out the dehydration of buten-2-ol-1, $CH_3.CH : CH.CH_2OH$, at 400–450°.

Piperylene.—Penten-2-ol-4 was prepared by means of the Barbier-Grignard[3] reaction from crotonaldehyde and methyliodide. 130 g. of the alcohol were distilled over kaolin at 400–420° and 60–75 mm. A mixture of carbondioxide and ether was used as a freezing mixture for condensing the hydrocarbon. The water of dehydration amounted to 27 cc., theory calls for 27.5 cc. The crude organic product. collected amounted to 75% of the theoretical. This was dried and fractioned through a column. The liquid on refractionation boiled at 41–44° and weighed 60 g. Reif[4] gives 40–41° as the boiling point of the hydrocarbon. The total high boiling residues from 130 g. alcohol used did not weigh more than 5 g.

It would seem that the decomposition of the alcohol was nearly theoretical. For a purer product the reaction must necessarily be carried out at lower pressures.

Hexadiene-2,4, $CH_3.CH : CH.CH : CH.CH_3$.—The alcohol[5] was prepared from crotonaldehyde and ethylmagnesium bromide. One hundred grams of hexenol were decomposed under the same conditions as the piper-

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

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

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

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

[5] Reif, *Ber.*, **39**, 1603 (1906).

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.

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

By L. P. KYRIAKIDES.

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

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

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

[3] Vorländer, Ber., 30, 2266 (1897).