and to the solubility of the alkaline constituents of the glass, and hence it must frequently be renewed. A similar color with methyl orange obviously may be produced by aqueous solutions of other acids or acid salts of suitable concentration. Of these, monopotassium and monosodium phosphate are particularly well adapted for the purpose, since the acidity of solutions of these substances is affected relatively slowly by the addition of acids or alkalies. Although the dissociation constant of the second hydrogen of phosphoric acid, 2×10^{-7}, is nearly identical with that of the first hydrogen of carbonic acid, 3×10^{-7}, the acidity of a solution of monosodium phosphate is somewhat less than that of an *equivalent* solution of carbonic acid, owing possibly to hydrolysis. Comparison of the color of a saturated aqueous solution of carbon dioxide, containing methyl orange, and solutions of monosodium phosphate of various concentrations, also containing methyl orange, shows that the carbonic acid solution is perceptibly less acid than a phosphate solution containing 20 g. of crystals[1] in 100 g. of water, more so than one containing 15 g. of crystals in 100 g. of water, while a solution of 17.5 g. of crystals in 100 g. of water possesses apparently the same color as the carbonic acid solution. An equivalent solution of monopotassium phosphate, containing 15.3 g. of crystals[2] was found to be identical in color with the solutions of the sodium salt. Since the hydrogen ion concentration of a carbonic acid solution changes only from about 2.5×10^{-4} to 1.2×10^{-4} between the limits of 0.2 normal and 0.05 normal, and since this difference in the hydrogen ion concentration corresponds to only 0.06 cc. fifth normal hydrochloric acid in 100 cc., and since, by escape of carbon dioxide, more concentrated solutions tend to approach a concentration of tenth normal, it is obvious that the above end point can safely be used in the titration of solutions from half to tenth normal.

Before being used, both salts should be crystallized to free them from phosphoric acid or disodium phosphate. Owing to its lesser solubility, the potassium salt is somewhat more easily purified and therefore better adapted for the purpose.[3] GREGORY PAUL BAXTER.

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OBSERVATIONS ON SOME BARBIER-GRIGNARD REACTIONS.

BY L. P. KYRIAKIDES.

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Methylethylethylene chlorhydrin: Chloro - 1 - methyl - 2 - butanol - 2, $CH_3.CH_2.C(CH_3)(OH).CH_2Cl$.—The chlorhydrins are usually obtained by the addition of hypochlorous acid to the unsaturated hydrocarbons.

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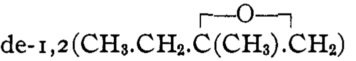
[1] $NaH_2PO.2H_2O$. This hydrate crystallizes between 41° and 0°. Imadsu, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, 3, 257 (1912).

[2] KH_2PO_4.

[3] This was pointed out to me by Dr. H. H. Willard.

M. Tiffeneau[1] has prepared some of the unsymmetrical chlorhydrins by the action of organomagnesium compounds on chloroacetone. In a paper on these preparations, he observes that he obtained chloro-1-methyl-2-butanol-2, with a yield of 72%, by the action of ethylmagnesiumbromide on chloroacetone. In a later paper by Fourneau and Tiffeneau[2], we read that the substance, described in the latter's previous paper, with the boiling point 149–151°, was not a homogeneous compound. They discovered that the reaction product consisted of a mixture of two compounds, both boiling at identically the same temperature; so that they could not be separated by fractional distillation. One of these substances was the normal Barbier-Grignard reaction product, boiling at 152–153°. The by-product consisted of ethyl-2-pentanol-3, $CH_3.CH(CH_2.CH_3).CH(OH).CH_2.CH_3$, boiling at 150°. This latter substance must have been formed by the action of the organomagnesium compound on either methyl-2-butylene-oxide-1,2$(CH_3.CH_2.\overbrace{C(CH_3).CH_2}^{O})$ or its metamer, methylethylacetaldehyde $(CH_3.CH_2.CH(CH_3).CHO)$ either of which might have been formed from the chloroalcohol during the reaction. The authors separated the two compounds by transforming the chlorhydrin to the oxide, whose boiling point is much lower than that of the alcohols.

Having discovered that oxides could be easily dehydrated to the corresponding hydrocarbons with conjugated double bonds, we undertook the study of Tiffeneau's synthesis. We were soon confronted with the fact that the yields of oxide, obtained by the treatment of the crude Barbier-Grignard reaction product with potassium hydroxide, varied within wide limits. In fact, at times it seemed that the side products were the main result of the reaction. These variations were found to be due to thermochemical causes. As the heat evolved in the action of chloroacetone on ethylmagnesium bromide is very great, local heating plays a prominent part during the reaction.

The Barbier-Grignard reaction is therefore carried out as follows: 67 g. magnesium turnings are put in a 2 1/2 liter bottle provided with a condenser and then covered with 750 cc. dry ether. The Grignard reagent is prepared by gradually adding a solution of 307 g. ethylbromide in 300 cc. dry ether. The reagent is treated with 400 cc. more ether, cooled by means of ice and salt to below —10°, and treated slowly, at such a rate that the drops can be counted, with a solution of 250 g. chloroacetone in 250 cc. ether. The bottle is kept in vigorous motion during the addition, which takes about 1 1/2 hours. The freezing mixture is renewed several times, in order to keep the temperature of the reaction mixture as low as possible. In this way, the addition product is obtained in

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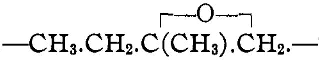
[1] *Compt. rend.*, 134, 774 (1902).

[2] *Ibid.*, 145, 437 (1907).

pulverulent form, floating throughout the liquid. The vigorous shaking, besides, hinders the addition product from falling into lumps and enclosing any of the free Grignard reagent. The reaction product prepared in this way is almost colorless, having at most only a very light yellow tinge. After the addition of the chloroacetone, the condenser is taken off, the bottle is stoppered, the latter shaken for a short time, and left in ice for an hour or two. The decomposition of the products is effected with ice and dilute acetic acid. The ethereal solution is washed several times with water, shaken with powdered calcium carbonate, dried over calcium chloride, and the ether distilled off through a column, until the water bath attains a temperature of 90–95°.



Methyl-2-butyleneoxide-1,2—$CH_3.CH_2.C(CH_3).CH_2$.—The residue obtained above, after distilling off the ether, is cooled with ice-water and treated slowly, while shaking, with a cold solution of 220 g. potassium hydroxide in 150 cc. water. After a short shaking, the upper layer is separated, dried over potassium carbonate, and the oxide is obtained by fractional distillation through a column. The aqueous alkaline layer is shaken once with a little ether, the ethereal layer dried, and fractioned separately. The crude oxide fractions are united and refractioned. The fraction boiling 78–85° is collected as oxide. This fraction, boiling mostly at 80–83°, weighed over 150 g., and contained traces of the metameric methylethylacetaldehyde. The yield of oxide was, therefore, over 65% of the theoretical on the magnesium originally used.[1] As the oxide is easily hydrolyzed, it is possible that some of it may have been transformed to the corresponding glycol, which might have been present in the residues from the oxide. These residues were not studied, further than that some small amounts of Fourneau and Tiffeneau's compound—ethyl-2-pentanol-3—could be isolated.

It is the belief of the writer that, by more efficient cooling and shaking of the Grignard reagent during the addition of the chloroacetone, the yield of methylchlorobutanol, and consequently that of the oxide, can be further increased.

Barbier-Grignard Reactions with Ethylchloride.—As far as I know, ethylchloride has not been hitherto used in ordinary organomagnesium reactions. Spencer and Mary Crewdon[2] describe the action of magnesium on ethylchloride at 260°, whereby they obtain a mixture of gases, consisting of butane, olefines and hydrogen.

As the use of ethylchloride instead of the bromide would be more advantageous on the large scale, I have thought of making use of it in preparing

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[1] As in the preparation of the Grignard reagent, 5 g. of magnesium had not gone in solution, the yield of oxide would be 68%.

[2] *Chem. Zentr.*, 1909, I, 146.

the Grignard reagent. The results obtained were excellent. The reagent was prepared as follows: 77 g. magnesium, in a 2-liter thick-walled bottle, were covered with 1 liter dry ether, and treated with a crystal of iodine and 1 cc. methyl iodide. The bottle was then cooled in ice-water and 34 g. ethylchloride were condensed in the ether. The bottle was closed tightly with a rubber stopper carrying a thermometer, whose bulb dipped within the ether, and the latter was warmed at its boiling point for some time. The liquid was then cooled down and about 60 g. ethyl chloride were condensed in it. The solution was then warmed again, and the process repeated until in all about 220 g. of the chloride had been added. This amount of the chloride is a little more than the theoretical amount required by the magnesium used. The metal is very smoothly and rapidly attacked, once the reaction is made to begin. In this preparation about 5 g. of the metal were left unattacked. It is to be observed that, as this reaction was carried out in a closed vessel, there would be no appreciable loss of ether or ethylchloride.

The Grignard reagent was cooled and treated with a solution of 275 g. chloroacetone—equivalent to 72 g. magnesium—in an equal volume of ether. In spite of the fact that this addition was not carried out very carefully, I obtained 153 g. of methylethylethyleneoxide from the crude reaction product. This amount of the oxide corresponds to about 60% of the theoretical yield on the chloroacetone used.

A similar reaction between ethylmagnesium chloride and acetone gave over 70% of tertiary amylalcohol—$(CH_3)_2C(OH).CH_2.CH_3$.

One of the advantages of using ethylmagnesiumchloride in the preparation of methyl-2-butylene oxide-1,2, is the fact that the addition product with chloroacetone is much more soluble in ether than the ethylbromide product. With the proportions of substances used in the example above, there is no separation of any solid products. In this case, therefore, the liquids can be cooled much more easily and local heating can be better avoided.

It has been our experience that Barbier-Grignard reactions give normal results, as a rule, when the addition of the substances containing the carbonyl group to the Grignard reagent is carried out slowly, with constant shaking and very efficient cooling. This has already been noted in the case of chloroacetone, where, because of the mobility of the chlorine atom, there is a marked tendency for abnormal reactions.

Kohler[1], having carried out a great number of organometallic reactions with unsaturated ketones, observes that the Grignard reagent has a marked tendency to add itself at the double bond. In these cases he obtained, besides the normal reaction products—the unsaturated tertiary alcohols—

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[1] *Am. Chem. J.*, 38, 511 (1907).

also varying quantities of the saturated ketones. These two products are the results of two reactions taking place simultaneously, namely:

$$\text{I. R.CH : CH.CO.R} + \text{R}_1\,\text{MgX} = \text{R.CH : CH.C(RR}_1\text{).OMgX} \longrightarrow \text{R.CH : CH.C(RR}_1\text{)(OH).}$$

$$\text{II. R.CH : CHCOR} + \text{R}_1\text{MgX} = \text{(RR}_1\text{)CH.CH : CROMgX} \longrightarrow \text{(RR}_1\text{)CH.CH}_2\text{.COR.}$$

R may stand for an alkyl or an aryl residue.

Kohler, on the basis of the results he obtained, concluded that the relative amounts of the final products in these organometallic reactions depend upon "the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues, the character of the magnesium derivative, and *possibly, temperature, concentration*[1] and solvent."

In his experiment with ethylidene acetone and methylmagnesium bromide, Kohler, having used two molecules of the magnesium compound to one of the ketone, obtained a product which consisted 75% of methylisobutylketone and only 25%, at most, of the normal reaction product—methyl-2-penten-3-ol-2. He isolated and determined the ketone after oxidizing the unsaturated alcohol with dilute permanganate solution.

Gry[2], on the other hand, observes that the interaction of equimolecular quantities of methylmagnesiumiodide and ethylidene acetone resulted in the formation of considerable quantities of the unsaturated tertiary alcohol —$CH_3.CH : CH.C(CH_3)_2(OH)$. He also states that, although he obtained products with high boiling point, he "did not encounter any ketonic products." Comparing the statements and the results of the above quoted authors, one would assume that the difference in results lay in the relative amounts of the Grignard reagents used in each case.

As unsaturated alcohols—especially those with a tertiary hydroxyl group—are easily dehydrated to doubly unsaturated hydrocarbons, we undertook the preparation of methyl-2-penten-3-ol-2 by means of the Barbier-Grignard reaction.

The reagent ($1^1/_2$ mol) was prepared as usual from magnesium and methyliodide in dry ether. It was then cooled by a freezing mixture to below —10°. The ethereal solution of ethylidene acetone (1 mol) was added slowly to the reagent, while the latter was kept in vigorous motion. The reaction mixture was left at room temperature for a short time, and then decomposed with ice and dilute acetic acid. The ethereal solution and the extracts were shaken with dilute sodium hydroxide solution, dried over potassium carbonate, and the ether distilled off through a column. The residue was fractioned *in vacuo*. We obtained in this way over 80% of the theoretical yield (on the ketone used) of a liquid that boiled at about

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[1] The italics are mine.

[2] *Bull. soc. chim.*, [4] 3, 377 (1908).

80° at 145 mm. The residues from this liquid showed signs of dehydration, and were not studied any further.

In order to determine the nature of the distilled product, we made use of a method of mine, which I shall describe in a later paper, whereby the tertiary alcohol could be quantitatively dehydrated to the corresponding diethylenic hydrocarbon.

On dehydrating the liquid, the dehydration products were found to consist to the extent of 75% of a doubly unsaturated hydrocarbon, whose constitution is very probably $CH_3.CH : CH.C(CH_3) : CH_2$. and not $CH_3CH : C : C(CH_3)_2$ as given by Gry.[1] This hydrocarbon boils at 76–77°—Gry gives its boiling point as 76–79°. The residues from the hydrocarbon consisted mostly of the tertiary alcohol itself, which was carried over by the water of dehydration during the distillation of the reaction products. This was proven to be the case by treating the above residues in the same way as the original liquid. By repeating this dehydration process we were able to transform practically all of the Barbier-Grignard reaction product to the hydrocarbon. From a total of 40 g. unsaturated alcohol used, we could obtain barely 1 g. of a liquid, which could be identified as methylisobutylketone.

The reaction, therefore, seems to have proceeded normally:

$$CH_3.CH : CH.COCH_3 + CH_3MgI = CH_3CH : CHC(CH_3)_2OMgI \longrightarrow CH_3CH : CHC(CH_3)_2(OH).$$

From the above results it would seem that the concentration of the Grignard reagent does not have any appreciable effect on the course of the reaction. If it were otherwise, both Gry and I ought to have had considerable amounts of methylisobutylketone. The reaction in all three cases was carried out by the gradual addition of the ketone to the ethereal solution of the organometallic compound. In every case, therefore, the magnesium compound was in great excess at the beginning of the reaction.

Hence, if concentration played any important part, the final results in all three cases ought to have been of the same nature. In the experiment described above, I had $^1/_2$ mol of the Grignard reagent in excess, and yet the result was not anywhere comparable with that obtained by Kohler. There can be no doubt, as Kohler asserts, that the course of the Barbier-Grignard reaction is influenced by the character of the reacting components. There must be other conditions, however, which influence the reaction very markedly.

I am of the opinion that efficient cooling,[2] and vigorous shaking during

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[1] *Bull. soc. chim.*, [4] **3**, 377.

[2] These observations agree with those of Latham Clarke in the reaction between saturated ketones of fairly high molecular weight and organomagnesium compounds [THIS JOURNAL, **34**, 680 (1912)].

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.

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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).