warming the mixture. The hydrazone separated in orange needles. When the mixture had cooled thoroughly, the crystals were filtered out, washed with dilute acetic acid, and recrystallized from alcohol. Fine orange needles resulted, which sintered at 185° and gave a clear melt at 194.° Yield, 0.19 gram.

0.1147 g. substance: 10.15 cc. N_2 (21° and 773.5 mm. over H_2O). Calcd. for $C_{23}H_{23}O_5N_3$: N, 9.97%. Found: N, 10.00%.

3. Summary.

1. The study of methoxylated carbinols has been extended by an investigation of a series of carbinols obtained by the action of various magnesium reagents upon trimethylgallic ester.
2. The 3,4,5-trimethoxytriphenyl carbinol has been found to be more strongly basic than triphenyl carbinol, but less so than *p*-methoxytriphenyl carbinol.
3. The trimethoxyphenyl dialkyl carbinols are generally unstable, losing water readily to form the olefin; whereas the trimethoxyphenyl dibenzyl carbinol is quite stable.
4. The action of isoamyl magnesium iodide upon trimethylgallic ester appears to follow a somewhat abnormal course, giving an unidentified by-product, in addition to the olefin.
5. Trimethoxyphenyl-diethyl and -dibenzyl methyl chlorides are very unstable.
6. A series of olefins of the type $(CH_3O)_3C_6H_2.CR : CHR$ have been prepared, and it has been shown that these substances do not form stable dibromides. Certain of these hydrocarbons show marked exaltation in molecular refraction.
7. A series of new 3,4,5-trimethoxyphenyl ketones has been obtained and examined.
8. New syntheses are recorded of 3,4,5-trimethoxy cinnamic acid, of syringic acid and of 3,4,5-trimethoxy acetophenone.

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SOME ORGANIC PREPARATIONS.

BY L. P. KYRIAKIDES.

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During the past three years we have had the occasion to use many organic reactions, and as the result of our study, we have been able to improve some of them.

The substances prepared and described are mainly related to the synthesis of the unsaturated hydrocarbons with conjugated double bonds, which of late years have become so important in the synthetic production of rubber-like masses.

Aldols.—These compounds have been known for quite a long time. They are usually prepared by condensing the aldehydes alone, or in mixture with other aldehydes, by means of alkaline bodies, especially carbonates. The best method known is that described by Grignard and Abelmann,[1] which consists in treating an ethereal solution of an aldehyde or a mixture of aldehydes with a solution of potassium hydroxide and stirring in the cold.

Acetbutyraldol, $CH_3.CH(OH).CH(CH_2.CH_3).CHO$.—This substance, as far as known to us, has not been prepared before. It is easily prepared by Grignard and Abelmann's[2] method. 160 g. freshly prepared acetaldehyde and 250 g. freshly distilled normal butyraldehyde are dissolved in 600 cc. ether. The solution is cooled to below 5° and treated slowly, while the condensation liquid is being stirred vigorously, with a 10% solution of potassium hydroxide. In all, about 70 cc. of the alkaline solution are used, the addition of which takes about 45 minutes. The liquid is stirred during the condensation continuously, and the temperature of the reaction mixture is never allowed to go above 10°. A good temperature is 5–7°. When it is observed that the liquid has no appreciable tendency to warm up, the reaction is assumed to be at an end. The aldol solution is separated from the alkaline layer, shaken several times with a little saturated sodium bicarbonate solution and dried over calcium chloride. After evaporating off the ether, the residue is distilled *in vacuo* from an oil bath. We have thus obtained 214 g. acetbutyraldol, boiling up to 110° at 24 mm. A redistilled sample boiled at 102–104° in the neighborhood of 20 mm. Acetbutyraldol is insoluble in water, but dissolves readily in ether and alcohol.

Acetaldol, $CH_3.CHOH.CH_2.CHO$.—This substance is easily obtained by using Grignard and Abelmann's method, although these authors have not described its preparation. In another article, Grignard and Reif[3] describe the preparation of acetaldol by treating an ethereal solution of acetaldehyde with an aqueous solution of sodium sulfite in the cold. In Grignard and Abelmann's process, which we have applied to the preparation of acetaldol, the results were excellent—the temperature of condensation being about 7°. Using acetone as diluent instead of ether, we have obtained very good yields of exceptionally good aldol. It might be supposed that in this latter condensation there might be some hydracetylacetone also formed, by the interaction between acetaldehyde and the acetone. On decomposing the aldol into the unsaturated derivative however, we could obtain very little, if any, ethylidene acetone, which tends to prove that in this condensation there is no appreciable forma-

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[1] *Bull. soc. chim.*, [4] 7, 638 (1910).

[2] *Ibid.*

[3] *Bull. soc. chim.*, [4] 1, 114.

tion of hydracetylacetone. The amount of acetone used as diluent was less than twice the volume of acetaldehyde taken.

In our further study of the aldol condensations, we have been able to dispense with the use of solvents altogether.

One of the drawbacks in these condensations is the fact that the aldehydes and aldols are usually very sensitive towards the alkalies, so that there is more or less resinification during the reaction. The older experimenters avoided this trouble, partially, by using weak alkaline compounds to effect the condensation; while of late the tendency has been to use strong alkalies in presence of inert organic solvents, which latter extracted continually the sensitive compounds from the sphere of action of the alkali.

It is noted by many that, in carrying out these condensations, the end of the reaction is judged by the appearance of a light yellow color in the aldol liquid. It has been our experience that this color is a sign of the formation of higher condensation products and resins. For a good aldol formation it is necessary that the liquid should be perfectly colorless.

A. F. McLeod,[1] in a paper on the condensation of acetaldehyde with formaldehyde states: "With calcium or sodium hydroxide solution of 0.1% either no condensation, or, only a very slow condensation of acetaldehyde occurred."

We have found, however, that it is very easy to condense acetaldehyde to acetaldol with amounts of sodium hydroxide equivalent to about 0.1–0.3% of the aldehyde used.

1 kilo freshly prepared acetaldehyde, in a long-necked 2-liter flask, is cooled to below 5°. The thermometer bulb must be within the liquid to be condensed, and the temperature carefully controlled during the reaction. To the cold acetaldehyde are now carefully added 5 cc. of a 10% sodium hydroxide solution, and the condensation carried on at 4–5°. The reaction mixture must be kept in brisk motion during the whole of the operation. After a short time, 5 cc. more of the alkali are added, and the process repeated, until in all about 20–25 cc. of the 10% sodium hydroxide solution have been added. This is perfectly soluble in the aldehyde-aldol. The addition takes about 20 minutes. The reaction liquid is then kept shaking at 4–5° for an hour more, after which it is made slightly acid with tartaric acid. The aldol is filtered from the salt, and distilled *in vacuo* from an oil bath, whose temperature is raised slowly. It was thus easy to obtain about 50% of the theoretical yield of acetaldol, the boiling point of which, on redistillation, was found to be 80° at 20 mm., and 72° at 12 mm. Part of the aldol is decomposed back into acetaldehyde during the distillation, as it has often been observed; otherwise the yield in non-distilled aldol varies between 70–80%

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[1] *C. A.*, 1, 717 (1907).

of the theoretical. It may be possible by increasing the time of reaction to obtain higher yields of aldol. The side products, such as higher condensation products and resins, do not amount to more than 1% of the aldehyde used, neither is there any crotonaldehyde formed. It might be noted here that the addition of some organic solvent, such as ether, facilitates the filtration of the aldol from the sodium tartrate.

For the control of the temperature during the condensation of the acetaldehyde it is advisable to have a freezing mixture ready. For most reactions it is not necessary to distil the aldols; it is sufficient to separate them from the free aldehydes by heating them for a short time *in vacuo.* As the rate of aldol condensation is a function of the concentration of the alkali, it stands to reason that the time of reaction can be varied by varying the amount of alkali used. In fact, an experiment with 0.12% of sodium hydroxide—percentage on the basis of aldehyde used—gave only 34% of distilled aldol, during a reaction of about one hour.

The method described above would be applicable to the preparation of the higher members of the series as these are, according to Grignard and Abelmann, relatively more stable in presence of the alkalies.

Unsaturated Aldehydes and Ketones.

These substances are usually obtained as by-products in the corresponding aldol condensations. They are also formed on heating the hydroxyaldehydes or hydroxy-ketones. We have been able to simplify the dehydration of these last named substances by generalizing known methods. The dehydration is effected by heating the aldol compounds with traces of a strong acid such as sulfuric acid or substances generally known as dehydrating catalytics, such as aluminum phosphate.

Crotonaldehyde, $CH_3.CH : CH.CHO$.—M. Delépine's[1] method of preparing this substance by treating paraldehyde with concentrated sulfuric acid is not very attractive. The method described by Grignard and Reif,[2] which consists in heating aldol in a flask provided with a column, is extremely slow and consequently tiresome. As a rule, the preparation of crotonaldehyde has not been very easy. Using, however, a catalyst, aldol can be easily dehydrated into crotonaldehyde.

The crude aldol from about 2500 g. acetaldehyde was put in a three-liter flask provided with an eight-bulb Young's column. The aldol was then treated with about 10 g. powdered aluminum phosphate and heated to boiling. The decomposition products boiling above 80° were collected for crotonaldehyde. The lower fractions contain acetaldehyde. The temperature of the distilling vapors soon attained the maximum of 100–105°. No appreciable residue was left in the flask, which, if present, is due to the resins formed in the aldol condensation.

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[1] *Compt. Rend.,* **147,** 1316 (1908).

[2] *Bull. soc. chim.,* [4] **1,** 114.

The distillate was saturated with calcium chloride, the organic liquid dried quickly over calcium chloride and fractioned through a column. We have been able to obtain 1225 g. crotonaldehyde, boiling at 98–102° C., or about 60% of the theoretical yield on the acetaldehyde originally used. It is easy by this method to dehydrate over a kilo of aldol in less than three hours.

Ethylidene Acetone, $CH_3.CH : CH.CO.CH_3$.—This substance also is said to be formed on long heating of hydracetylacetone. It is also obtained on heating the latter substance with acetic anhydride.[1] It is easily prepared catalytically.

400 g. hydracetylacetone—$CH_3.CH(OH).CH_2.CO.CH_3$—are treated with two drops of concentrated sulfuric acid and distilled from a flask provided with a column. The distilling vapors attain the maximum temperature of about 120°. There is some acetone and acetaldehyde in the low boiling fractions. The distillate is treated with potassium carbonate, the organic layer dried over the same drying agent and fractioned through a column. Ethylidene acetone boils at 122°. In a similar way mesityl oxide can be prepared from diacetone alcohol by using aluminum phosphate or better still, sulfuric acid—a few drops of the acid to a kilo of the ketone alcohol (compare Moritz Kohn).[2]

The diacetone alcohol we have prepared by using barium hydroxide as the condensing agent. The alkali was put in a Soxhlet apparatus and the acetone boiled on a steam bath for several days until the liquid stopped boiling. A little tartaric acid was added to the acetone at the beginning of the reaction, in order to neutralize any barium hydroxide carried down from the Soxhlet apparatus, either mechanically or in solution. A. Hoffman[3] uses calcium hydroxide for condensing acetone to diacetone—alcohol. · Barium hydroxide being a stronger alkaline substance, comparable in its alkalinity to the alkali hydroxides, increases the rate of condensation.

Glycols of the Hydrocarbons.

These substances are usually prepared by the reduction of the corresponding hydroxy-aldehydes and hydroxy-ketones with aluminum amalgam. In some cases they have been prepared by the reduction of ketone alcohols with sodium amalgam. We have discovered that dihydroxyl compounds can be easily obtained by the electrolytic reduction of the corresponding aldol bodies. Since our discovery, we have seen a patent,[4]

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[1] *Ber.*, **25**, 3166.

[2] *Chem. Zentr.*, **1913**, II, 577.

[3] THIS JOURNAL, **31**, 722.

[4] Eng. Pat. 940 of Jan. 13, 1913; see also *C. A.*, **7**, 3242 and *Soc. Chem. Ind.*, **1913**, 550.

assigned to the Farbenfabriken of Elberfeld, which deals with a method identical with ours. The reduction is effected as follows:

Butandiol-1,3, $CH_3.CH(OH).CH_2.CH_2OH$.—Twenty-five grams of acetaldol, distilled *in vacuo*, were dissolved in 100 cc. of water, and then treated with a cold solution of 10 cc. concentrated sulfuric acid in 20 cc. of water. The solution thus made served as the cathode liquid and was poured within the porous cup of an electrolytic cell. The anode liquid consisted of a 10% aqueous sulfuric acid. The electrodes were made of lead. The cathode consisted of a spiral through which cold water was kept running. The effective cathode surface was 125 cm^2. The aldol solution within the porous cup was kept in motion by a mechanical stirrer moving within the loops of the lead spiral. The temperature of the cathode liquid during electrolysis was below 15°. The aldol solution was electrolyzed for 4 hours and 30 minutes, at a potential of 4 volts and a current strength of about 6 amperes—ND_{100} = 5 amperes. After electrolysis the cathode liquid was neutralized and saturated with potassium carbonate, and extracted five times with a mixture of ether and alcohol. The ether-alcoholic solution was dried over potassium carbonate, the solvents distilled off and the residue fractioned *in vacuo*. We collected 18 g. substance boiling between 105 and 120° at 20 mm. The major portion of the glycol distilled over at 110–114° at the same pressure. The total high boiling residue was less than 2 g. The glycol, distilled at ordinary pressures, boiled at about 205°. The yield of glycol was therefore nearly 70% of the theoretical. For most purposes, the crude aldol, obtained after treatment *in vacuo* to free it from acetaldehyde, can be electrolyzed directly in a 10–15% aqueous sulfuric acid as a 20% aldol solution. The yields vary between 40–50% of the theoretical.

Ketone alcohols can be reduced in a similar manner to the corresponding dihydroxy-compounds. Thus, an aqueous solution of crude methyl-2-butanon-3-ol-1, made by the condensation of methylethylketone with formaldehyde, gave about 35% of methyl-2-butandiol-1,3, on electrolyzing in a 10% sulfuric acid solution, as with acetaldol.

Aldols are also easily reduced to the glycols in a manner similar to Zelinsky and Ujedinoff's[1] reduction of hydracetylacetone to pentandiol-2,4. The acetaldol, being reduced in this way, gave over 80% of pure butandiol-1,3.

Pinacone, $(CH_3)_2C(OH).C(OH)(CH_3)_2$.—This substance is easily prepared by the methods of Holleman,[2] or Richard and Langlais,[3] which consist in treating acetone with magnesium amalgam.

As calcium is so closely allied to magnesium in many of its reactions,

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[1] *J. prakt. Chem.*, **84**, 545 (1911).

[2] *Rec. trav. chim.*, **25**, 206 (1906).

[3] *Bull. soc. chim.*, [4] **7**, 454 (1908).

we have attempted to reduce acetone to pinacone with calcium amalgam. As, however, calcium oxide is a strongly alkaline substance as compared with magnesium oxide, the side products obtained in the reduction are more abundant. H. D. Law and F. M. Perkin[1] have observed that metallic calcium acting on acetone at ordinary temperatures induces the formation of mesityl oxide together with higher condensation products. At higher temperatures the amount of high condensation products increases correspondingly.

43 g. calcium were amalgamated with 800 g. mercury. The amalgamation required long heating because of a layer of calcium oxide on the surface of the metal turnings. The cold calcium amalgam was treated with 400 cc. of acetone and the mixture boiled for more than 24 hours on the steam bath. The flask was shaken occasionally in order to break the amalgam. Because of this massive lump the amalgam had not all reacted. The reaction mixture was treated with 45 g. water, boiled, filtered, and the precipitate extracted twice with boiling acetone. The liquid was distilled until the vapors attained the temperature of 95°. The residue was treated with 100 cc. water, inoculated with a crystal of pinacone hydrate and left in the ice-chest. The liquid was filtered off from the crystals, the latter were washed with cold water, then with benzol and dried by pressing between filter papers. The pinacone hydrate thus obtained weighed about 50 g. The yield of the substance was therefore more than 20% of the theoretical.

We have tried to carry out this reduction in presence of an inert organic solvent but the results were poorer, if anything.

Because of the relative cheapness of production of calcium as compared with magnesium, the study of this reduction of acetone with calcium amalgam to pinacone might be worth while.

Conclusions.

Aldol condensations can be effected by means of the alkali hydroxides, even in the case of aldehydes which are very sensitive towards these hydroxides. Where weak alkalies have heretofore been used, these can be replaced by the alkali hydroxides, only in the latter case the amount of the condensing agent must, naturally, be much smaller. The relative amounts of the different alkalies can be determined by comparing their dissociation constants.

Aldols and ketone alcohols can be reduced to the corresponding dihydroxy-compounds electrolytically in a sulfuric acid solution, preferably at a lead cathode, or in a way similar to Zelinsky and Ujedinoff's reduction-method of hydracetylacetone to pentandiol-2,4.

Pinacone can be obtained by the reduction of acetone with calcium amalgam.

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[1] *Chem. Zentr.*, **1908**, (I), 1610.

In conclusion, I wish to express my thanks and indebtedness to my colleague, R. B. Earle, for assistance in the study of these reactions and many valuable suggestions.

CAMBRIDGE, MASS.

THE PREPARATION OF DIGLYCERIDES.[1]

BY R. R. RENSHAW.

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The preparation and isolation of the diglycerides is an unusually difficult task, for several reasons. In the most fruitful methods of preparation, there is always obtained a mixture of the di- and triglycerides, as well as free fatty acids and possibly small quantities of the isomeric diglycerides.[2] These products do not differ greatly in solubility or crystallizability, and some of them are exasperatingly alike in these properties. The melting points of all of them are close together, and some have double melting points. The problem is complicated, too, on account of considerable disagreement in the data afforded by the literature.[3]

The following methods for the preparation of the 2,3-diglycerides are theoretically possible:

1. By the direct action of the fatty acid on glycerol or the monoglycerides at higher temperatures.[4] It has been supposed that the 1,3-

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[1] Presented in part at the forty-fifth general meeting of the American Chemical Society, Washington, D. C., Dec. 28, 1911.

[2] It is possible that the diglyceride may also form with the free acid present stable double compounds. Grün and Schacht (*Ber.*, **40**, 1786 (1907)), have isolated from the action of myristic acid on glyceryl disulfate a compound to which they have assigned the formula $C_3H_5(OH)(OCOC_{13}H_{27})_2 + 2C_{13}H_{27}COOH$.

[3] A typical example is illustrated in the glycerides of stearic acid.

Stearic acid melts at 69.2°. It is readily soluble in ethyl ether, and in cold petroleum ether.

1-Monostearin melts at 73° (Guth, *Z. physiol. Chem.*, **26**, 83 (1902)); 78° (Kraft, *Ber.*, **34**, 4343 (1903)). It is sparingly soluble in cold ethyl ether and in cold petroleum ether.

2,3-Distearin melts at 72.5° (Guth); 76° and remelts at 58°, and after several months' standing at 74.5° (Grün, *Ber.*, **36**, 2286 (1905)); **38**, 1781 (1907)); 76.5° (Hundeshagen, *J. prakt. Chem.*, **28**, 219). It is sparingly soluble in cold ethyl ether and in cold petroleum ether.

1,3-Distearin melts at 74.5° (Guth); 78.2° (Grün and Theimer, *Ber.*, **38**, 1995 (1907)). The author has confirmed the latter. This glyceride is sparingly soluble in cold ethyl ether, and in cold petroleum ether.

Tristearin melts at 71 to 71.5° and remelts at 55° (Guth). It is sparingly soluble in cold ethyl ether, and in cold petroleum ether.

The same relationship as regards solubility holds for these substances in other solvents.

[4] For the preparation of the stearins by this method, see Berthelot, Vol. 2, p. 67; Hundeshagen, *J. prakt. Chem.*, **28**, 227 (1883).