magnesium.   The salts studied by Ephraim may be arranged in a series showing the relative amounts of ammonium salts needed to prevent precipitation if a base is added.   This explanation of the action of ammonium salts in preventing the precipitation of the hydroxides of bivalent metals is advanced in place of the usual theory of repression of the electrolytic dissociation of ammonium hydroxide by ammonium salts, as bringing the reactions into line with other equilibrium reactions, and as considering the solvent (including thereby dissolved substances) as the predominating influence in the reaction.   These reactions are now being studied quantitatively from this point of view and the results will be communicated later.

It is evidently possible to apply similar views to other reactions.   No more will be taken up here in detail, but only the view will be emphasized that chemical reactions need not be considered to depend upon electrolytic dissociation.   With the atoms in a molecule all carrying electric charges, certain properties of a solvent make some of these charges evident to experimental methods, while certain, perhaps very often the same, properties of the solvent increase the extent or rate of a reaction.   These phenomena are independent of each other but both dependent upon the solvent, or possibly some other underlying cause.   Many of the changes which have been considered heretofore as metatheses involve, without doubt, primary addition and subsequent decomposition or splitting off in various ways of the reacting molecules.

NEW YORK, N. Y.

USE OF IODINE AS A DEHYDRATING AND CONDENSING AGENT.

BY HAROLD HIBBERT.
Received May 3, 1915.

The question of devising some simple general method for the dehydration of organic hydroxy compounds has recently (on account of its importance in connection with the rubber synthesis) been made the subject of considerable activity among chemical investigators, as is indicated by the numerous patents taken out on this subject.   In the interesting communication of Kyriakides[1] on the "Preparation of Butadiene—1 : 3 Hydrocarbons," some valuable data are quoted to show that the dehydration of various glycols and alcohols can be readily brought about in the "wet way" by heating them with a small amount of a mineral acid of high dissociating power.   It would seem that the use of such a reagent offers many advantages over that of such substances as sulfuric acid,[2] potassium

[1] THIS JOURNAL, 36, 980, 987 (1914).

[2] The use of phosphoric acid for the preparation of unsaturated derivatives (Newth, J. Chem. Soc., 79, 917 (1901)), has so many advantages over sulfuric acid that it is difficult to understand why this reagent is not more frequently employed.

bisulfate, oxalic acid, zinc chloride, aluminum chloride, etc., since the formation of by-products is thereby almost entirely avoided. This author explains the dehydrating action of such acids as being due to a primary ester formation followed by a subsequent dissociation of this into halogen acid and unsaturated derivative. A very small amount of mineral acid suffices in this way for the dehydration of a large amount of the carbinol or glycol, respectively. Of considerable interest is the fact that the salts of these acids with weak bases are also equally efficient in bringing about such decompositions. Due to the stable character of the halide esters derived from primary alcohols, the method was found to be inapplicable to these compounds.

Some two years ago it was found by the writer that the marked disadvantages associated with the majority of such condensing agents could be avoided, and highly satisfactory yields of unsaturated derivatives obtained, by heating the hydroxy compound with a minute quantity of iodine. Thus diacetone alcohol when heated alone under ordinary pressure boils around $164°$, though with considerable decomposition, acetone being formed.

$$(CH_3)_2 : C(OH).CH_2.CO.CH_3 = 2CH_3.CO.CH_3.$$
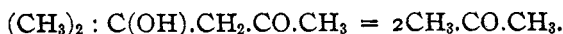
When mixed, however, with as small a quantity as $1/10,000$ part of iodine, and then distilled, it breaks down into water and mesityl oxide, practically a theoretical yield of the latter being obtained.

$$(CH_3)_2 : C(OH).CH_2.CO.CH_3 = (CH_3)_2 : C : CH.CO.CH_3 + H_2O.$$
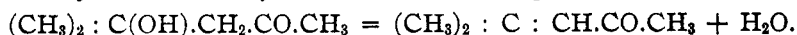
The reaction has, in fact, been found to be capable of general application. Further, in presence of a small amount of iodine, tertiary amyl alcohol on heating yields amylene; pinacone is converted into dimethylbutadiene, and cyclohexanol into tetrahydrobenzene. Under the influence of the same reagent, glycols yield polyglycols; glycerol is transformed into polyglycerols and condensation between aldehydes and glycols is readily brought about.[1]

Theory of the Process.

It is of interest that the ease of decomposition is found to vary in a marked manner with the nature of the alcohol employed. Thus while tertiary alcohols, on heating with small amounts of iodine, lose water very readily, this decomposition takes place, in general, much more slowly with the secondary, and scarcely at all with the primary derivatives. On the one hand, tertiary amyl alcohol (ethyldimethylcarbinol), pinacone, and diacetone alcohol all decompose with the greatest ease into water

[1] Recent experimental work carried out at this Institute by my colleague Benjamin T. Brooks has shown that the reaction is also applicable to a variety of dehydration phenomena in the terpene series. This data will appear in a forthcoming issue of THIS JOURNAL.—H

and unsaturated derivative, while with a secondary alcohol such as cyclohexanol the formation of tetrahydrobenzene takes place very slowly.

How are we to explain the remarkable effect produced by such small amounts of iodine?

If we call to mind the fact that the action of iodine on a metallic hydroxide results in the primary formation of an iodide and hypoiodite

$$2KOH + I_2 = KOI + KI + H_2O$$

and assume that organic (alkyl) hydroxides (in other words, alcohols) may possibly function in a similar manner, then in the case of dimethylethylcarbinol mentioned above, this in presence of iodine, might also be expected to yield a mixture of iodide and hypoiodite:

$$2(CH_3)_2 : C(OH).CH_2.CH_3 + I_2 = (CH_3)_2 : CI.CH_2.CH_3 + (CH_3)_2 : \\ C(OI).CH_2.CH_3 + H_2O$$
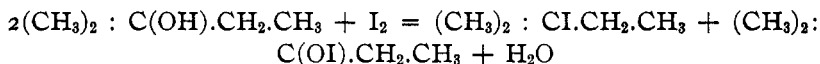
Now it is a well-known fact that the majority of alkyl halides dissociate to a greater or less extent at or below their boiling point, and of these the iodides represent the most unstable derivatives. Thus, in the case of all alkyl iodides we have at least a partial decomposition[1] on heating into olefine and hydriodic acid, so that with the iodide in question we should have some dissociation taking place as indicated by the equation:

$$(CH_3)_2 : CI.CH_2.CH_3 \rightleftharpoons (CH_3)_2 : C : CH.CH_3 + HI$$
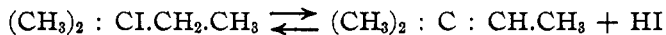
and presumably the hypoiodite, being much more unstable would dissociate even more readily.

$$(CH_3)_2 : C(OI).CH_2.CH_3 \rightleftharpoons (CH_3)_2 : C : CH.CH_3 + HOI.$$

The interaction of the two acids HI and HOI would, however, give water and iodine,

$$HI + HOI = H_2O + I_2,$$
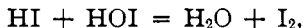
the latter then reacting again as shown in Equation 1. In this way we have a continuous cycle of reactions (in which the iodine functions as a catalytic agent), resulting in the formation of two final products, *viz.*, water and the unsaturated derivative. It would seem that the reactions just outlined are capable of being applied to any tertiary, secondary or primary alcohol, and the theory apparently offers a simple explanation of the part played by the iodine in reactions of allied types. Since, in general, the stability of the alkyl iodide and hypoiodite increases from the tertiary through the secondary to the primary derivative, it is to be expected that the iodine will function more readily with tertiary alcohols of the type of pinacone than with secondary, such as cyclohexanol, and this in fact has been found to be the case. The method is apparently inapplicable to the primary alcohols on account of the much more stable character of the corresponding alkyl iodides.

[1] It is scarcely necessary to point out that a *partial* decomposition is all that is required by the theory under discussion.

In general, it may be said, that the presence of iodine should facilitate the splitting off of water from any organic compound in which one of two adjacent carbon atoms has a hydroxyl (OH) group, the other, a hydrogen atom attached to it.

Written in a general form this would be indicated by

$$\begin{array}{cc} H & OH \\ | & | \\ R-C-C-R'-H_2O & = R-C=C-R'. \\ | & | \end{array}$$

Further, according to this theory, the ease of splitting off of the water should be dependent on the ease with which the iodide

$$\begin{array}{cc} H & I \\ | & | \\ R-C-C-R' \\ | & | \end{array}$$

is capable of dissociating into unsaturated hydrocarbon and HI

$$\begin{array}{cc} H & I \\ | & | \\ R-C-C-R' \longrightarrow R-C = C-R' + HI, \\ | & | \end{array}$$

which in turn is dependent on the greater or less labile nature of the H atom. Thus it may be assumed that an alcohol of the type

(A)
$$\begin{array}{ccc} H & OH & H \\ | & | & | \\ R-C-C-C-R' \\ | & | & | \\ H & H & H \end{array}$$

would give with iodine the iodide (B) and hypoiodite (C)

(B)
$$\begin{array}{ccc} H & I & H \\ | & | & | \\ R-C-C-C-R' \\ | & | & | \\ H & H & H \\ (3) & (2) & (1) \end{array}$$

(C)
$$\begin{array}{ccc} H & (OI) & H \\ | & | & | \\ R-C-C-C-R' \\ | & | & | \\ H & H & H \\ (3) & (2) & (1) \end{array}$$

and whether hydrogen would split off from carbon atom (1) or (3) would depend on the relative affinity between it and the respective carbon atom. If this were the same, or approximately the same, we should expect to get from the alcohol (A) equal quantities of the two isomers (D) and (E).

(D)
$$\begin{array}{c} H \\ | \\ R-C=C-C-R' \\ | \quad | \quad | \\ H \quad H \quad H \end{array}$$

and

(E)
$$\begin{array}{c} H \\ | \\ R-C-C=C-R' \\ | \quad | \quad | \\ H \quad H \quad H \end{array}$$

In the case of diacetone alcohol

$$\begin{array}{ccccc} (CH_3)_2:C(OH).CH_2.CO.CH_3 \\ 5 \quad\; 4 \quad\quad 3 \quad\; 2 \quad 1 \end{array}$$

we should expect that the presence of the negative carbonyl group would render the hydrogen atoms attached to carbon atom (3) more labile than those attached to carbon atom (5) so that mesityl oxide
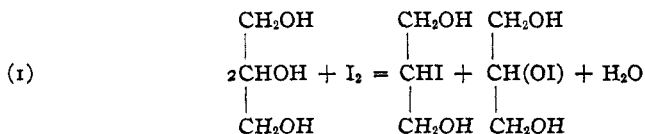
$$(CH_3)_2:C:CH.CO.CH_3$$

and little or none of the isomer
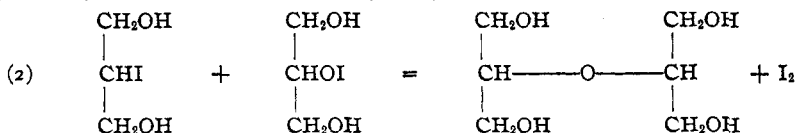
$$CH_2:C.CH_2.CO.CH_3$$
$$|$$
$$CH_3$$
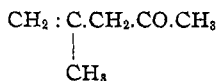
should be obtained.

The behavior, however, on redistillation (p. 1756) of the anhydrous distillate obtained by heating diacetone alcohol with a small quantity of iodine seems to indicate the presence of some of this second derivative.

While the above theory would thus appear to offer a good working hypothesis, it is quite possible that the alkyl iodide and hypoiodite react *directly* without undergoing a previous dissociation, and such a view would seem to offer a ready explanation of the action of iodine in bringing about the condensation of glycols to polyglycols and of glycerol to polyglycerol. Since, as indicated above, a secondary alcohol is more reactive than a primary, presumably on heating glycerol with iodine, the secondary alcohol group will be the one to react, with the formation of an iodide and hypoiodite.

$$
\begin{array}{lll}
CH_2OH & CH_2OH & CH_2OH \\
| & | & | \\
(1) \qquad 2CHOH + I_2 = & CHI + & CH(OI) + H_2O \\
| & | & | \\
CH_2OH & CH_2OH & CH_2OH
\end{array}
$$

In presence of the two negative hydroxyl groups it seems possible that the iodide and hypoiodite might function exactly as HI and HOI, respectively, and thus react directly to give oxide and free iodine

$$
\begin{array}{llll}
CH_2OH & CH_2OH & CH_2OH & CH_2OH \\
| & | & | & | \\
(2) \quad CHI & + \quad CHOI & = \quad CH\text{——}O\text{——}CH & + I_2 \\
| & | & | & | \\
CH_2OH & CH_2OH & CH_2OH & CH_2OH
\end{array}
$$

the iodine then reacting again as in Equation 1.

It is of interest that, as shown by Kyriakides,[1] the action of small amounts of strongly dissociating acids such as HCl, HBr, HI on glycols results in the formation of unsaturated alcohols or hydrocarbons, or both, depending on the conditions employed, while when iodine is employed as the dehydrating agent the principal product, as shown later, is a polyglycol, although undoubtedly some of the unsaturated alcohol is also obtained.[2] This would seem to indicate that in the case of these substances

[1] *Loc cit.*

This point is to be investigated later.

a *direct* decomposition between the alkyl iodide and hypoiodite takes place as indicated above, and would seem to provide evidence for the assumption that, in the cases where iodine is employed as the condensing agent, both types of reaction may take place depending on the nature of the compound in question.

In the condensation of glycols with aldehydes, for example, of butylene glycol with acetaldehyde, an apparently simple explanation of the manner in which the iodine functions would seem to lie in the assumption of the primary formation of an addition compound of the aldehyde and iodine

$$CH_3.CHO + I_2 = CH_3.CH{<}^{OI}_{I}$$
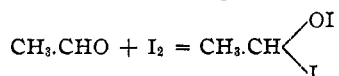
and that this then reacts with butylene glycol to give 1-methylpropane-diol-ethylal, water and iodine

$$CH_3.CH{<}^{OI}_{I} + {}^{HO.CH_2}_{CH_2}_{HO.CH.CH_3} = CH_3.CH{<}^{O-CH_2}_{CH_2}_{O-CH-CH_3} + H_2O + I_2.$$
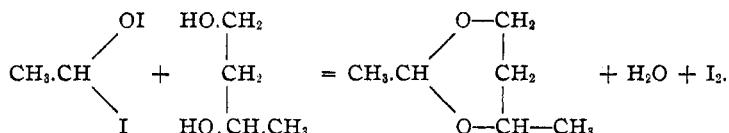
If the above theory is correct, then since the iodine plays the part of a *direct* catalyzer (cf. Rosanoff, "Outline of a Theory of Homogeneous Catalysis"),[1] in all such reactions it should obey "the law of mass action." Some indication that this is the case is obtained from the experiments on the condensation of glycerol (pp. 1760–1761), and further work is being undertaken to confirm this view.

Experimental Part.

This has been divided so as to embrace the following groups:

I. Synthesis of unsaturated hydrocarbons from alcohols.
II. Synthesis of unsaturated ketones from ketone alcohols.
III. Synthesis of unsaturated aldehydes from aldols.
IV. Synthesis of polyglycols and polyglycerols.
V. Condensation of glycols with aldehydes.

Group I.—Synthesis of Unsaturated Hydrocarbons from Alcohols.

(*a*) **Preparation of Trimethylethylene from Tertiary Amyl Alcohol.**— Sixty grams of tertiary amyl alcohol ($C_2H_5.C(OH) : (CH_3)_2$), b. p. 101–102°, were mixed with 0.14 g. of iodine and the product heated on the steam bath for about 24 hours, using a distilling flask and glass beads, the side tube of the flask being connected with a reflux condenser. There was a steady decomposition of the alcohol into the corresponding amylene (trimethylethylene). The distillate, after drying with calcium chloride, was redistilled and yielded about 27 g. of a product, b. p. 35–39° (principally 36–37°). Trimethylethylene, $CH_3.CH : C : (CH_3)_2$, boils at 39°.

[1] THIS JOURNAL, **35,** 173 (1913).

The residue in the flask consisted of the unchanged tertiary amyl alcohol.

(b) **Synthesis of Dimethyl Butadiene from Pinacone.**—A small quantity of pinacone was prepared by reducing acetone with magnesium amalgam, according to the method of Hollemann.[1] On completion of the reaction the product was distilled with steam and the pinacone hydrate obtained in solid form by cooling the aqueous distillate to around o°. This was dehydrated by leaving over night in a vacuum desiccator over sulfuric acid, during which period considerable volatilization took place, 9 g. of the hydrate yielding only 5 g. of pinacone.

Preparation of Dimethyl Butadiene.—Five grams of pinacone were transferred to a small flask, mixed with 0.012 g. iodine, and distilled slowly over the naked flame, using a fractionating column. A rapid decomposition took place when the temperature of the outer bath reached 140°. The product distilling over (weight approximately 3 g.) was dimethyl butadiene, which on redistillation boiled at 69–72°. (According to the literature, dimethyl butadiene boils at 69.5°.) It combined with bromine with great readiness, yielding a crystalline tetrabromide melting around 135°.

Several attempts were made to prepare dimethyl butadiene from pinacone hydrate by heating this product with small traces of iodine, but only poor yields of the unsaturated hydrocarbon were obtained. Thus, while pinacone itself, in presence of a relatively small amount of iodine, goes over very readily on heating into dimethyl butadiene, the presence of water, in the form of the hydrate, seems to prevent this reaction from proceeding except to a limited degree, and it was invariably found that pinacone distilled over with the water, recombining in the distillate to form pinacone hydrate.

(c) **Preparation of Tetrahydrobenzene from Cyclohexanol.**—Twenty-seven grams of cyclohexanol were mixed with one-fiftieth its weight of iodine, and the product heated in a distilling flask (the neck of which was filled with glass beads to serve as a fractionating column) to about 170–175° for about 60 hours. The distillate (amounting to 21 g.) separated into two layers. After removal of the lower aqueous portion and drying the upper layer with calcium chloride, about 18 g. remained, from which, on a subsequent fractionation under ordinary pressure, about 7–8 g. of pure tetrahydrobenzene, b. p. 82–84° were isolated.

The method is of interest in view of the fact that a patent on the preparation of synthetic rubber substitutes, by passing the vapors of cyclohexanol over heated platinum or other contact material, has been taken out by the Badische Company.

Possibly the above process could be utilized for the preparation of tetrahydrobenzene on the commercial scale, and it would seem that better

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

yields of the unsaturated rubber hydrocarbons should be obtained from this, than by the use of cyclohexanol itself.

Group II.—Synthesis of Unsaturated Ketones from Ketone-Alcohols.

Preparation of Mesityl Oxide from Diacetone Alcohol.—It was stated in the introduction that diacetone alcohol, when distilled under ordinary pressure, boils around 164°, undergoing, however, considerable decomposition into acetone. In presence of a small quantity of iodine, the reaction proceeds in an entirely different manner, mesityl oxide being obtained in a practically quantitative yield.

Expt. I.—700 g. of diacetone alcohol were mixed with 0.5 g. of iodine ($= 0.07\%$) and the product distilled under atmospheric pressure over the naked flame, using a short fractionating column filled with glass beads. The thermometer in the column indicated a temperature of 90° after the first few drops had distilled over, and remained there until about one-third the distillate had been collected. After about two-thirds had distilled over the remaining distillate was collected separately and found to be free from water, consisting in fact of practically pure mesityl oxide, b. p. 125–130° (principally 128–130°). The remaining two-thirds of the distillate consisted of two layers, and after removing the lower aqueous portion, the upper layer was dried with calcium chloride and refractioned.

Fraction 1.	B. p. 60° to 80°	6 g.
Fraction 2.	B. p. 80° to 125°	47 g.
Fraction 3.	B. p. 128° to 130°	259 g.
		312 g.

The aqueous layer, after being saturated with potassium carbonate, yielded 11 g. of an oil consisting of equal parts of acetone and mesityl oxide. The total yield of mesityl oxide (consisting of everything boiling between 80° and 130°) was 578 g., representing a yield of 97.8% crude mesityl oxide.

Expt. II.—A further experiment was carried out using 200 g. of diacetone alcohol and 0.02 g. iodine (representing 0.01% or 1 part in 10,000) and in this case also practically a theoretical yield of mesityl oxide was obtained.

It then seemed of interest to determine whether the method is applicable to mixtures of diacetone alcohol and acetone. Using the above quantity of iodine (*viz.*, 0.01 to 0.02% calculated on the weight of diacetone alcohol present) it was found that on distillation the greater part of the acetone distilled over below 80°, the further distillation then resulting in the decomposition of the diacetone alcohol into mesityl oxide and water which proceeded exactly as indicated in the above experiments.

In every case a few cc. of a dark-colored oil remained in the flask, which however, did not give any reaction indicating the presence of free iodine.
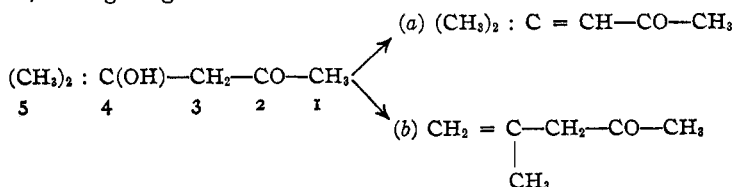
It was thought that possibly the presence of this product would suffice to bring about the catalytic decomposition of a fresh quantity of diacetone alcohol, without the further addition of iodine, but on carrying out such an experiment by introducing a fresh quantity of diacetone alcohol and distilling, little or no decomposition into mesityl oxide occurred.

The mesityl oxide as thus obtained is a clear, colorless product and quite free from diacetone alcohol as shown by the following experiment:

100 g. of the product, b. p. 120° to 130°, were shaken four times, using 20 cc. of water for each operation and the remaining oil dried with calcium chloride and redistilled. There were obtained 95.7 g. of mesityl oxide, b. p. 120–130°.

From the boiling point, physical properties, etc., there is no doubt that the method gives a practically pure product and thus represents an especially simple and inexpensive process.

It was pointed out in the previous discussion that the decomposition of diacetone alcohol might very well proceed simultaneously in two directions, thus giving rise to two isomeric substances:

$$(a)\ (CH_3)_2 : C = CH-CO-CH_3$$

$$(CH_3)_2 : C(OH)-CH_2-CO-CH_3$$
$$\quad 5 \qquad 4 \qquad 3 \quad 2 \quad 1$$

$$(b)\ CH_2 = C-CH_2-CO-CH_3$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad CH_3$$

Owing, however, to the proximity of the carbonyl group it was thought that the hydrogen atoms attached to carbon atom (3) would prove to be much more labile than those attached to carbon atom (5) so that relatively little of (B) would be formed. Curiously enough it was found that a quantity of a lower boiling product (b. p. 80–125°) was always obtained. After carefully drying this product and submitting it to a re-distillation the boiling point invariably rose with each successive re-fractionation, so that eventually it was completely converted into mesityl oxide, as indicated in the following typical experiment:

Six hundred grams diacetone alcohol were mixed with 0.2 g. iodine, and the mixture distilled over the naked flame at ordinary pressure, using a fractionating column and glass beads.

> Fraction (1).[1]   70–125°.................. 370.4 g.
> Fraction (2).   125–130°.................. 144.3 g.
> Fraction (3).   130–131°.................. 28.1 g.
> ──────────
> 542.8 g.

(These temperatures are those indicated on the thermometer in the neck of the distilling flask.)

[1] No record was kept of the amount distilling over below 70° and of the residue left in the flask.

Treatment of Fraction I (B. P. 70–125°).

After separating off the water, the product was shaken four times with water (50 cc. for each operation) in order to remove any acetone and diacetone alcohol; there was little or no loss in this operation.

After drying with calcium chloride, it was redistilled under ordinary pressure, using glass beads.

Weight of product taken = 248.0 g.

Fractions............ (1)a 71–120°   (2)a 120–125° (3)a 125–128° (4)a 128–131°
                      34.6 g.   25.0 g.   32.7 g.   155.7 g.

Fractions (1)a, (2)a, and (3)a were then redistilled with the following results:

Refractionation of (1)a: B. p. 71–120°. Wt., 34.6 g.

   (1)b below 120°   (2)b 120–127°   (3)b 127–130°
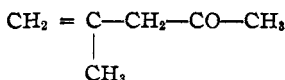   18.0 g.   2.6 g.   14.0 g.

Refractionation of (2)a: B. p. 120–125°. Wt., 25.0 g.

   (1)b below 120°   (2)b 120–125°   (3)b 125–131°
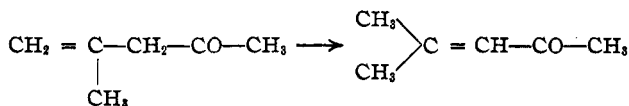   3.4 g.   3.2 g.   18.4 g.

Refractionation of (3)a: B. p. 125–128°. Wt., 32.7 g.

  (1)b below 120° (2)b 120–125° (3)b 125–128° (4)b 128–131°
   1.1 g.   0.9 g.   6.0 g.   24.7 g.

It will be noted that in each case the boiling point of the distillate has risen appreciably, approaching more closely to that of mesityl oxide. This would seem to point to the probable presence of the second isomer:

$$CH_2 = C-CH_2-CO-CH_3$$
$$|$$
$$CH_3$$

which on distillation goes over into mesityl oxide:

$$CH_2 = C-CH_2-CO-CH_3 \longrightarrow \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} C = CH-CO-CH_3$$
$$|$$
$$CH_3$$

That a mixture of acetone and mesityl oxide behaves quite normally on distillation under ordinary pressure is indicated by the following experiment:

13 g. acetone with 13 g. pure mesityl oxide were distilled together under ordinary pressure, using a fractionating column.

Fractions........ (1) B. p. 58–73°   (2) B. p. 73–127°   (3) 127–130°
                   10.5 g.   3.2 g.   12.0 g.

This shows that the presence of the acetone exercises little or no effect in lowering the boiling point of the mesityl oxide, and further that no mixture of constant boiling point exists.

Group III.—Synthesis of Unsaturated Aldehydes from Aldols.

Preparation of Crotonaldehyde from Acetaldol and Paracetaldol.— The various processes described in the literature for the preparation of crotonaldehyde by direct distillation of acetaldol[1] give relatively poor yields (averaging about 50%, calculated on the weight of aldol taken) and the same remark applies to those methods involving the use of dehydrating agents, for example, potassium bisulfate.

The addition of a small quantity of iodine to the aldol, prior to the distillation, increases the yield of crotonaldehyde in a remarkable manner, as is shown in the following experiments:

Expt. I.—50 g. pure *paracetaldol* were distilled slowly from a small flask in the course of one hour, using a short fractionating column filled with glass beads. At the commencement of the distillation the thermometer in the neck of the column at once rose to 95°, remaining near this temperature almost throughout the experiment. An attempt to increase the rate of distillation caused the thermometer to rise at once to 140°, indicating only a partial decomposition into crotonaldehyde and water. The residue in the flask weighed about 7 g. The distillate, after separating off the water, was dried with CaCl₂, a further small quantity of crotonaldehyde being recovered by saturating the aqueous solution with the same reagent. The crude product weighed 27 g. On redistillation there were obtained:

Fractions.... I. 60–97° II. 97–104° (principally 100–104°) III. (above 104°)
                2 g.   22 g.   2 g.

This represents a yield of some 55% crotonaldehyde, a considerable portion of the paracetaldol being decomposed into acetaldehyde.

Expt. II.—150 g. *acetaldol* were distilled under the same conditions as described in Expt. I. It was found that the product could be distilled rapidly without the thermometer going above 95°. A considerable quantity of liquid distilled over between 65–95°. After drying with CaCl₂ for 2–3 hours the crude product weighed 92.5 g. On refractionation there were obtained:

Fractions.... I. 40–70°   II. 70–96°   III. 96–104°   IV. Residue
                13.0 g.   25.5 g.   47.0 g.   3.0 g.

No attempt was made to collect the product coming over below 40°. Fractions I, II, and III were again dried with CaCl₂ (I and II showed evidence of the presence of moisture, III was apparently quite dry) and redistilled.

Fraction I was found to consist principally of acetaldehyde.

Fraction II yielded four fractions:

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[1] Orndorff and Newbury, *Monatsh. Chem.*, **13**, 516 (1892); Grignard and Reif, *Bull. soc. chim.*, [4] **1**, 114 (1907); McLeod, *Am. Chem. J.*, **37**, 30 (1907).

(*a*) below 70° (principally 21–40°)   (*b*) 70–97°   (*c*) 97–104°   (*d*) above 104°
    6.0 g.   6.0 g.   10.5 g.   3 g.

Total amount of crotonaldehyde obtained was $47.0 + 10.5 = 57.5$ g., equivalent to a yield of 49%.

Effect of the Addition of a Small Quantity of Iodine.—Expt. III.— 80 g. of pure *paracetaldol* were mixed with 0.08 g. iodine and distilled under the conditions described above, the entire operation occupying some 30 minutes. The thermometer in the column never indicated above 95°, and the residue left did not amount to more than about 7 g. After drying the distillate with $CaCl_2$ for 2–3 hours it was redistilled and found to boil very constantly at 100–104°. The distillate amounted to 52 g., equivalent to a yield of 82%, which, considering the mechanical losses, must be regarded as highly satisfactory. It was apparently a very pure product.

Expt. IV.—A similar experiment was carried out by distilling 200 g. *acetaldol* with 0.1 g. iodine over the naked flame. The operation took about two hours, the residue left in the flask amounting to 15 g. After drying with $CaCl_2$, the crude product (wt. = 134 g.) was redistilled.

           Fractions................ I. 65–96°   II. 96–105°
                            14.0 g.   114.5 g.

Fraction I was again dried and redistilled and then yielded 10 g. crotonaldehyde, b. p. 96–104°. The total weight of crotonaldehyde, b. p. 96–104° (principally 102–104°) obtained amounted to 124.5 g., corresponding to a yield of 80%.

In the course of these experiments several interesting facts relative to the behavior of crotonaldehyde came to light. It was found that a small quantity of water has the effect of lowering the boiling point of this substance appreciably, as shown in the following experiment:

To 100 g. of pure crotonaldehyde (b. p. 102–104°) was added 0.5 g. water and the mixture distilled, using a fractionating column and beads:
Fractions............. I. below 98°   II. 98–102°   III. 102–104°
                       2.5 g.   30.5 g.   67 g.

Another point which calls for attention is the fact that whereas with *acetaldol* a lower boiling fraction (b. p. 65–96°) was always obtained along with the crotonaldehyde, this was not the case with paracetaldol. This lower boiling fraction, after very careful drying to remove all the water present, invariably decomposed on distillation, yielding a further quantity of acetaldehyde and crotonaldehyde, so that after several fractionations it was decomposed completely into these two products. The same phenomenon occurred when a large quantity (several hundred grams) of *well-dried* crotonaldehyde, b. p. 98–102° (that is, 2–4° below the true boiling point) was submitted to a careful refractionation. This gave a large amount of product boiling at a somewhat higher temperature, *viz.*, 102–104°, and a considerable quantity, b. p. 98–102°. This latter on being

submitted to fractionation for a third time yielded some acetaldehyde, the product commencing to distil over below 30°, while a considerable quantity (about 17%) was collected between 85–98°. This latter also on refractionation gave a further quantity of pure crotonaldehyde, b. p. 102–104°.

It is an interesting speculation as to whether we are not dealing here with a compound of crotonaldehyde with acetaldehyde of the type

$$CH_3.CH : CH.CH \underset{O}{\overset{O}{\diamond}} CH.CH_3,$$
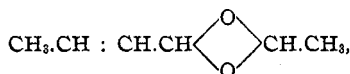
which decomposes into crotonaldehyde and acetaldehyde on repeated distillation. The fact that acetaldol gives rise to this lower-boiling mixture, while paracetaldol does not, is perhaps to be connected with the relatively greater ease of dissociation of the former back again into acetaldehyde.

The above body would be analogous to the one formed from acetaldol and acetaldehyde, whose benzoyl derivative,

$$CH_3.CH(O.CO.C_6H_5).CH_2.CH \underset{O}{\overset{O}{\diamond}} CH.CH_3,$$
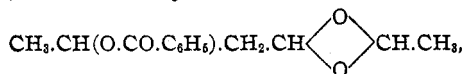
was obtained by P. C. Freer[1] by the action of sodium on acetaldehyde and benzoyl chloride in ether solution.

There would also seem to be an indication of the actual existence of the parent substance,

$$CH_3.CHOH.CH_2.CH \underset{O}{\overset{O}{\diamond}} CH.CH_3,$$
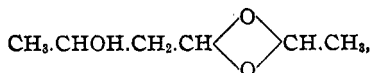
in the fact that the distillation of the crude product obtained by the condensation of acetaldehyde to acetaldol by various alkaline reagents, under widely varying conditions, almost invariably gives a yield of approximately 66% aldol, and 33% acetaldehyde, thus pointing to the probable existence of this in the condensation product, and to its decomposition

$$CH_3.CHOH.CH_2.CH \underset{O}{\overset{O}{\diamond}} CH.CH_3 \longrightarrow CH_3.CHOH.CH_2.CHO + CH_3.CHO.$$
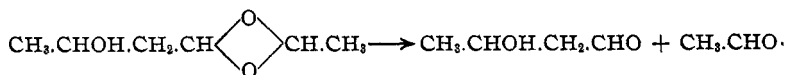
on heating.

These experiments will be described in a later communication.

Group IV.—Synthesis of Polyglycols and Polyglycerols.

(a) **Preparation of Polyglycol from Butylene Glycol.**—200 g. of butylene glycol were mixed with 1.0 g. iodine and heated in a distilling flask, using a fractionating column, for about 8 hours in an oil-bath, the temperature of the latter being so regulated that the thermometer in the distilling flask never showed a temperature higher than about 130°. About 80

[1] *Ann.*, **293**, 326 (1896).

g. distilled over, consisting apparently of crotyl alcohol, water and some other by-products. The residue in the flask was then distilled under reduced pressure, and after about 20–30 g. of butylene glycol had passed over at 175°, under a pressure of 20–25 mm., the temperature rose rapidly to about 200°, the remainder (about 80 g.) distilling over between 200–350°, under the above pressure. The product was not examined further, but consisted presumably of polyglycols.

(b) **Syntheses of Polyglycerols.**—The following examples are typical of a number carried out under somewhat similar conditions:

Experiment I.—1518 g. C. P. anhydrous glycerol were mixed with 1/3000 of its weight (0.506 g.) iodine and the product heated in an oil bath at ordinary pressure for 7 hours, the flask being connected with a condenser. A slow stream of carbon dioxide was passed through the apparatus throughout the experiment, the temperature of the oil bath being maintained at 210–215°. During this period 120 g. of distillate were obtained, principally water with some glycerol.

The remaining product was then distilled under reduced pressure with the following result:

Fraction (1) Aqueous distillate passing over at ordinary pressure....... = 120.0 g.
Fraction (2) Water + glycerol (below 184° at 23 mm.).............. = 82.0 g.
Fraction (3) Glycerol, b. p. 169° at 5 mm........................... = 592.0 g.
Fraction (4) Glycerol and polyglycerol, b. p. 169–183° at 4 mm........ = 265.0 g.
Fraction (5) Glycerol and polyglycerol, b. p. 183–226° at 4 mm........ = 113.0 g.
Fraction (6) Polyglycerol, b. p. over 226° at 4 mm.................. = 346.0 g.

$$\overline{\qquad\qquad}$$
1518.0 g.

On account of the difficulty in separating polyglycerol from glycerol, no accurate estimate of the yield can be made, but assuming that Fractions 5 and 6 represent a diglyceride, this would represent some 33% by weight of that of the glycerol originally taken. In an attempt to isolate a constant-boiling product, Fraction 6 was redistilled under reduced pressure. The temperature rose rapidly to 235° at 5 mm. and 195 g. distilled over between 235–284° with the pressure gradually rising from 5 to 31 mm. A third refractionation of the 195 g. thus obtained gave

Fraction (1)   27.0 g. below 234° at 5 mm.
Fraction (2) 122.0 g. 234–240° at 3–5 mm. (principally 234–236 at 3 mm.)
Fraction (3)   46.0 g. above 240° at 3 mm.

Experiment II.—814 g. of C. P. anhydrous glycerol were mixed with 1/3000 of its weight (0.271 g.) iodine and heated for 1 hour at ordinary pressure under the same conditions as described in Expt. I, the temperature of the oil bath being 210–215°. It was then heated for one hour under reduced pressure (45–55 mm.) at the same temperature, after which the product was distilled under reduced pressure.

Fraction (1) Water and glycerol...................................   =   78.0 g.
Fraction (2) Glycerol, b. p. 169° at 5 mm.........................   = 450.0 g.
Fraction (3) Glycerol and polyglycerol, b. p. 170–220° at 3 mm.......   = 145.0 g.
Fraction (4) Polyglycerol, b. p. 220–237° (principally 225–235° at 3 mm.)   =   87.0 g.
Fraction (5) Residue..   =   54.0 g.
                                                                      ─────────
                                                                        814.0 g.

The somewhat lower boiling point of the polyglycerol obtained in Fraction 4 in comparison with Expt. I is probably due to the fact that in Experiment I a metal, and in Expt. II an oil bath was used for heating the flask during the distillation.

Experiment III.—457 g. C. P. anhydrous glycerol were mixed with 1/5000 of its weight (0.091 g.) of iodine and heated for 7 hours at ordinary pressure under same conditions as in Expt. I. At the end of this period the product was distilled under reduced pressure.

Fraction (1) Water and glycerol.....................   = 27 g.
Fraction (2) Glycerol, b. p. below 175° at 3 mm..........   = 312 g.
Fraction (3) Residue in flask.........................   = 109 g.

Apparently reducing the amount of iodine from 1/3000 to 1/5000 diminishes the yield appreciably, under the same conditions.

Experiment IV (Blank Experiment).—314 g. of C. P. anhydrous glycero were heated for 5 hours at ordinary pressure under same condition as in Expt. III. Only a few drops of water passed over and on distilling the product under reduced presssure it boiled constantly at about 170° at 8–10 mm. Not more than 5 g. of high-boiling product remained behind.

The experiment is of interest in bringing out more clearly the action of the iodine in facilitating the condensation.

Group V.—Condensation of Glycols with Aldehydes.

Preparation of 1-Methyl Propane-diol-ethylal.—Fifty grams of butylene glycol were mixed with 60 g. acetaldehyde, and 0.3 g. iodine added. The mixture was heated on the water bath, using a reflux condenser, for about 4–6 hours. The excess of acetaldehyde was then distilled off, using glass beads, and the fraction passing over between 40–180° redistilled after drying with potassium carbonate. 55.5 g. of a product, b. p. 110–125° (principally 118–120°) were abtained. This represents a yield of 86% of 1-methyl propane-diol-ethylal obtained by the condensation of one molecule of butylene glycol, with one molecule of acetaldehyde.

Presumably the quantity of iodine employed could be materially diminished, as well as the time of heating, and the yield could probably be increased.

The condensation is also brought about by the use of a small amount of 20% sulfuric acid.

Summary.

A description has been given of various experiments carried out illustrative of the use of iodine as a dehydrating and condensing agent.   In all the cases investigated, *viz.:*

(*a*) Conversion of alcohols into unsaturated hydrocarbons.

(*b*) Conversion of ketone-alcohols into unsaturated ketones.

(*c*) Conversion of aldols into unsaturated aldehydes.

(*d*) Conversion of glycols and glycerols into polyglycols and polyglycerols, respectively.

(*e*) Condensation of aldehydes with polyalcohols.

It has been found that a very small amount of iodine (in some cases as low as 1/10,000 part by weight) suffices to bring about the change.   The reaction is apparently a general one, and a tentative theory has been advanced to explain the catalytic role played by the iodine in such processes.

In two recent patents[1] the claim is made that the presence of small traces of iodine induces in a remarkable manner the condensation of amines with alcohols (*e. g.*, formation of dimethylaniline from aniline and methyl alcohol) as well as the splitting off of HCl from amines and their hydrochlorides, so that it would not be at all surprising if this reagent should prove capable of an extremely wide application in synthetic organic work both in the laboratory and in the industry.

PITTSBURGH, PA.

THE ACETOLYSIS OF CARBOHYDRATES.

BY S. BORN AND J. M. NELSON.

The study of the acetolysis of the carbohydrate part of invertase[2] led to the following work on the acetolysis of other carbohydrates.   It was hoped that by an extensive study of a large number of these disaccharides and polysaccharides, we might be able to formulate some general principle regarding the structure of these compounds from their behavior on acetolysis, and thus throw more light on the constitution of the carbohydrate part of invertase.

It has been noticed in the acetolysis of various disaccharides and poly-

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[1] Knoll and Co., D. R. P. 241,853, 250,326.

[2] THIS JOURNAL, **36**, 398 (1914).