THE SYNTHESIS OF POLYHYDRIC ALCOHOLS BY MEANS OF FORMALDEHYDE.[1]

BY H. HOSÄUS, P. RAVE, P. WIGAND, AND B. TOLLENS.

I. INTRODUCTION.

BY B. TOLLENS.

THE aldehyde of formic acid or of methyl alcohol, the formaldehyde CH_2O, which can be easily obtained in large quantities, and which at present is assumed to furnish the sugars in the vegetable kingdom by polymerization, is a very favorable material for the synthetic formation of polyhydric alcohols.

Formaldehyde possesses the property when added to other aldehydes or ketones in the presence of calcium or barium hydroxide of combining directly with these, forming compounds in which one or more primary alcohol groups (methyl according to the Geneva nomenclature) are present.

According to the experiments carried out by the above gentlemen and myself the carbon atoms combined with the aldehyde group COH or the ketone group CO of the bodies acting upon formaldehyde react by combining with as many CH_2O groups as there are hydrogen atoms united to them.

Probably formaldehyde and water form methylen glycol $CH_2(OH)_2$ and this condenses with the aldehydes or ketones with the separation of OH and H or water.

Thus CH_2 and $2CH_2O$ form $C(CH_2OH)$ and CH_3 with $3CH_2O$ forms $C(CH_2OH)_3$.

At the same time the aldehyde group COH becomes CH_2OH and the ketone group CO becomes CHOH. There are therefore two more atoms of hydrogen taken up, another portion of formaldehyde forming formic acid with the decomposition of a molecule of water.

As a result of these changes the following reaction takes place in the case of acetaldehyde:

$$\begin{matrix} CH_3 \\ | \\ COH \end{matrix} + 4CH_2O + H_2O = \begin{matrix} C-(CH_2OH)_3 \\ | \\ CH_2OH \end{matrix} + CH_2O_2$$

[1] Read before the World's Congress of Chemists, August 23, 1893.

a body being formed which contains four CH_2OH groups combined with one carbon atom or $C(CH_2OH)_4$.

Propionaldehyde, CH_3CH_2COH in which the carbon atom which is linked to the aldehyde group is combined with only two hydrogen atoms, forms CH_3, $C(CH_2OH)_2$, CH_2OH or

$$C\begin{cases}CH_3\\(CH_2OH)_3\end{cases}$$

Pyrotartaric acid $CH_3.CO.COOH$ forms

$$\left.\begin{array}{l}C—(CH_2OH)_3\\|\\CHOH\\|\\COOH\end{array}\right\}C_6H_{12}O_6$$

Levulinic acid, $CH_3.CO.CH_2.CH_2.COOH$, combines, as it contains a carbon atom with three hydrogen atoms and another with two hydrogen atoms linked to CO groups, with $5CH_2O$ groups forming

$$\left.\begin{array}{l}C—(CH_2OH)_3\\|\\CHOH\\|\\C(CH_2OH)_2\\|\\CH_2\\|\\COOH\end{array}\right\}C_{10}H_{20}O_8$$

The bodies thus formed from pyrotartaric and levulinic acids with formaldehyde are on account of the presence of the carboxyl group still acid and are further decomposed with the separation of water forming lactones or anhydrides. Thus pyrotartaric acid gives $C_6H_{10}O_5$ and levulinic acid $C_{10}H_{16}O_6$. (See below).

Acetone, $CH_3.CO.CH_3$, probably takes up $6CH_2O$ groups and forms

$$\left.\begin{array}{l}C(CH_2OH)_3\\|\\CHOH\\|\\C(CH_2OH)_3\end{array}\right\}C_9H_{20}O_7$$

or better according the analyses so far made $C_9H_{18}O_6$ a hepta-

tomic alcohol with nine carbon atoms which is partially an anhydride.

The reaction of formaldehyde upon aldehydes and ketones above described is probably general in the alcohol and fatty acid series and we are at present engaged in a further investigation which will no doubt furnish a greater number of polyhydric alcohols and alcohol acids.

II. DESCRIPTION OF THE PRODUCTS ABOVE MENTIONED.

(*a*) *Pentaerythrol*, $C(CH_2OH)_4$. (*Tetramethylolmethane*).

By B. Tollens, F. Wigand, and P. Rave.

This very interesting compound, which was first prepared some years ago[1] but has been investigated only lately crystallizes very beautifully and is formed by mixing

600 grams formaldehyde (32.4 per cent.),
60 grams acetaldehyde,
160 grams calcium hydroxide,
and 9 liters water.

The mixture is allowed to stand several weeks with frequent shaking. The liquid is then decanted, the calcium removed by precipitation with oxalic acid and upon evaporation and separation of the syrup from the crystals by filtration about 115 grams of crude pentaerythrol are obtained.

This is purified by repeated crystallization and extraction with alcohol and then melts at 250–255°. It shows all the properties of a tetrahydric alcohol with five carbon atoms, so that we chose the above name for it as an empirical homologue of erythrol.

As tetrahydric alcohol it forms a tetracetate and tetrabenzoate, with hydrobromic acid and a tri-and tetrabromhydrin, with hydriodic acid a di-, tri-, and tetraiodhydrin which all crystallize well and show definite melting points.

With nitric acid and with chromic acid it is decomposed and furnishes among other products glycolic acid but no acetic acid. With iodine and sodium hydroxide it does not form iodoform.

From these reactions and the fact that it does not form a secondary iodide with hydriodic acid (as for instance mannitol forms secondary hexyl iodide) we reason that the carbon atoms

[1] *Annalen der Chemie*, **265**, 315; **276**, 58.

in pentaerythrol are not regularly linked but that it possesses the structure of a methane in which the four hydrogen atoms are replaced by four CH_2OH groups.

(*b*) *Pentaglycerol* $C\begin{smallmatrix}/CH_2\\ \backslash(CH_2OH)_3\end{smallmatrix}$ (*Methyltrimethylolmethane*).

BY H. HOSÄUS.

When

20 grams propionaldehyde,
80 grams formaldehyde (40 per cent.),
1100 grams water,
and 50 grams calcium hydroxide

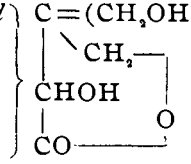
are heated on the water bath, pentaglycerol is formed.

$$\begin{smallmatrix}CH_3\\ |\\ C(CH_2OH)_2\\ |\\ CH_2OH\end{smallmatrix} \quad \text{or} \quad C\begin{smallmatrix}/CH_3\\ \backslash(CH_2OH)_3\end{smallmatrix}$$

The liquid is decanted, the dissolved lime precipitated with oxalic acid and the filtrate evaporated to a syrup which slowly crystallizes. The crystals show after purification the melting point 199° and prove to be a trihydric alcohol with five carbon atoms. Pentaglycerol upon distillation in vacuo yields at 165° a triacetate and a tribenzoate.

When oxidized with chromic acid it yields acetic acid and this proves that it contains a methyl group.

(*c*) *Lacton from pyrotartaric acid and formaldehyde.* (*Trimethylol lactic acid lacton*).



BY H. HOSÄUS.

By warming

27 grams pyrotartaric acid,
90 grams formaldehyde (40 per cent.),
70 grams calcium hydroxide,
and 1450 grams water

there is formed the calcium salt of a lactic acid in which three hydrogen atoms are replaced by three CH_2OH groups and by precipitation of the calcium with oxalic acid and evaporation of

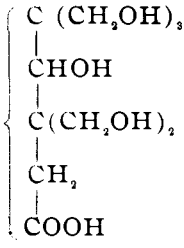
the filtrate this acid is changed into its lacton. After purification the crystals melt at 184°.

This lacton which is neutral regenerates the acid when boiled and combines with 1 molecule of NaOH or $\frac{1}{2}$ molecule of CaO.

It does not react with iodine and sodium hydroxide nor with phenylhydrazin and therefore does not contain any pyrotartaric acid.

(*d*) *Lacton from levulinic acid and formaldehyde.*

Anhydride of



BY P. RAVE AND B. TOLLENS.

We obtained the barium salt of this acid by allowing

50 grams levulinic acid,
250 grams formaldehyde (40 per cent.),
200 grams crystalline barium hydroxide,
and 5 liters water

to stand fourteen days with frequent shaking, then heating, carefully precipitating the barium with sulphuric acid and evaporating the filtrate. From the syrup we obtained the lacton $C_{10}H_{16}O_5$, crystallizing in small plates melting at 174–176°, the formula being controlled by Raoults method.

This compound reacts neither with iodine and sodium hydroxide nor with phenylhydrazin therefore containing no levulinic acid. It is almost neutral but combines with one molecule of NaOH on boiling. It is derived from hydrogenized levulinic acid or hydroxy-valerianic acid, being anhydro-pentamethylol-hydroxy-valerianic-acid-lacton and formed from the above acid by the loss of $2H_2O$.

When of the six hydroxyls contained in the above formula one forms a lacton by combining with the carboxyl with separation of H_2O and two others unite in a manner similar to an ether, only three hydroxyls remain, and it is a fact that upon heating this lacton with acetic anhydride three acetyl groups are introduced, a well crystallizing triacetate of the lacton being formed.