

*Citation:*

A.F. Holleman, Preparation of cyclohexanol, in:  
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it is evident that the harmonic curves of  $P$  with respect to the curves of the cubic pencil also form a system with index *two*.

For  $k^3$  passing through  $P$  the curve  $h^3$  breaks up into the system of the polar conic and the polar line of  $P$  with respect to that curve which touch each other in  $P$ .

As  $k^3$  and  $h^3$  have in common the tangents out of  $P$ , being thus of the same class, the harmonic curve has only then a node when this is the case with the original curve.

5. If with respect to a given  $k^3$  we determine on each right line through  $P$  the points  $B_1, B_2, B_3$  in such a way that  $B_i$  is harmonically separated by  $A_i$  from  $A_j$  and  $A_k$ , we get as locus of the points  $B$  a curve of order *six*,  $h^6$ , with a threefold point in  $P$ . For, if  $B_1$  coincides with  $P$ , then  $A_1$  is one of the points of intersection of  $k^3$  with the polar line of  $P$  and the reverse (see § 1).

As the points  $B$  correspond one by one to the points  $A$ , the curve  $h^6$  is of the same genus as  $k^3$ , so it has still 6 double points or cusps. This last is excluded because in that case not a single tangent could be drawn from  $P$  to  $h^6$ , whilst it is clear that the tangents out of  $P$  to  $k^3$  also touch  $h^6$ .

From the definition of  $h^6$  follows immediately that this curve can meet the curve  $k^3$  only in the points of contact  $R$  of the above mentioned six tangents: so in each point  $R$  they have three points in common. The right line  $PR$  having in  $R$  two points in common with  $k^3$ , but three points with  $h^6$ ,  $R$  must be one of the six nodes of  $h^6$  and  $PR$  one of the tangents in that node.

**Chemistry.** — "*Preparation of cyclohexanol.*" By Prof. A. F. HOLLEMAN.

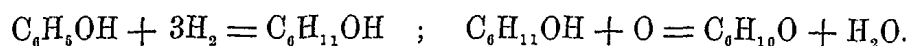
The preparation of ketohexamethylene in somewhat large quantities is one of the most lengthy operations, whatever known process may be used.

Since, by means of the addition of hydrogen to benzene, by the process of SABATIER and SENDERENS, hexa-hydrobenzene has become a readily accessible substance, it was thought advisable to use this as a starting point for the preparation of the said ketone by first converting it into monochlorohexamethylene, converting this in the usual manner into the corresponding alcohol and then oxidising this to ketone by the process indicated by BABYER. Mr. VAN DER LAAN has tried, in my laboratory to realise this.

The method, however, appeared impracticable as the chlorocyclohexane was not readily converted into the alcohol. MARKOWNIKOFF has tried to attain this by using alcoholic potash; we have tried it by shaking the said chloro-compound for several days and at different temperatures with silver oxide and water + alcohol, but a transformation worthy of the name was not controlled.

The chlorination of cyclohexane in quantities of 80—100 grams to the monochloro-compound was moreover a disagreeable and slow operation. The most satisfactory results were obtained by MARKOWNIKOFF's first method (A. 301, 184) by pouring the hydrocarbon on to water in a Drechsel flask and then passing chlorine into the water at 30—40°. The influence of light is very pronounced in this case. Direct sunlight causes explosion. If chlorine is passed through the hydrocarbon exposed to faint light it dissolves with a yellow colour. If now this solution is exposed to sunlight a violent evolution of hydrogen chloride takes place; in strong light this is accompanied by luminous phenomena.

MR. VAN DER LAAN, however, succeeded in readily preparing ketohexamethylene by another process. It appeared that phenol and hydrogen combine to hexahydrophenol by the method of SABATIER and SENDERENS and that the cyclohexanol obtained could then be oxidised to the corresponding ketone:



For the preparation of cyclohexanol  $\text{C}_6\text{H}_{11}\text{OH}$  a combustion tube was quite filled with nickeloxide which was then reduced by means of pure hydrogen. By means of an asbestos stopper, one end of the tube was connected with a wash-bottle containing phenol; this was placed in an airbath heated to 160—170°. The tube was placed in a combustion furnace in an iron gutter lined with asbestos. The bulbs of two thermometers were also placed in the gutter and the flames were so regulated that they showed 140—160°. By means of another asbestos stopper, the other end of the tube was connected with an adapter leading into a flask closed with a doubly-perforated cork. Through the second hole was passed a gas exit tube by means of which the absorption could be controlled.

The current of pure and dry hydrogen which was passed into the wash-bottle containing the phenol charged itself with vapour which in the presence of an excess of hydrogen was exposed to the catalytic action of the nickel.

In the receiver a liquid consisting of two layers collected, the bottom layer being water.

The top layer was submitted to distillation. From 85°—110° a liquid

distilled, which separated into two layers one of which consisted of water whilst the other had a bitter peppermint-like odour. From  $110^{\circ}$  the temperature rapidly rose to  $160^{\circ}$  and from  $160-180^{\circ}$  a considerable fraction passed over. What distilled above  $180^{\circ}$  was mainly unchanged phenol, which was again subjected to treatment with hydrogen. To remove any phenol, the fraction  $160-180^{\circ}$  was washed a few times with dilute soda-lye, the alkaline washings were shaken with ether to recover any dissolved cyclohexanol, the ether was evaporated and the residue united with the main liquid. After a few more distillations a liquid was obtained, perfectly clear and of a thick consistency, boiling at  $160-161^{\circ}$ , the b.p. of cyclohexanol being recorded as  $160^{\circ}.3$ . A combustion gave the following result. 0.1740 grm. gave 0.4610 grm.  $\text{CO}_2$  and 0.2017 grm.  $\text{H}_2\text{O}$ ; found:

C 72.2 H 12.8

calculated for  $\text{C}_6\text{H}_{12}\text{O}$ : C 72.0 H 12.0

By oxidation with BECKMANN'S chromic acid mixture (1 mol.  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\frac{1}{2}$  mol  $\text{H}_2\text{SO}_4$  in 300 grms. of water) of which 135 grams were used for 10 grams of hexanol and operating at a low temperature, hexanol gives a fair yield of ketohexamethylene.

Mr. VAN DER LAAN has not determined the exact amount of cyclohexanol obtainable from phenol but this is certain that the yield is quite satisfactory. If four tubes with nickelpowder are heated at the same time 1 kilo of hexanol may be easily prepared within 7 or 10 days.

As a result of this investigation some substances which were only accessible with the greatest difficulty, have now become easy of preparation. First of all cyclohexanol and ketohexamethylene. The latter may be nearly quantitatively oxidised to adipic acid and as its calcium salt gives a fair yield of ketopentamethylene when submitted to dry distillation, these two latter substances are no longer to be regarded as chemical curiosities.

*Groningen, Lab. Univs. September 1903.*

**Vegetable Physiology.** — "*Investigations of some xanthine derivatives in connection with the internal mutation of plants*". By Dr. TH. WEEVERS and Mrs. C. J. WEEVERS — DE GRAAFF. (Communicated by Prof. C. A. LOBRY DE BRUIN).

The investigations of CLAUTRIAU <sup>1)</sup> and of SUZUKI <sup>2)</sup> as to the function of caffeine have shown that this substance must probably be regarded as a decomposition ("Abbau") product of albumenoids.

<sup>1)</sup> G. CLAUTRIAU. *Nature et Signification des Alcaloides végétaux*, Bruxelles 1900.

<sup>2)</sup> SUZUKI. *Bull. Coll. Agric. Tokyo Imp. Univ. Vol. 4. 1901. pag. 289.*