

Citation:

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The equation

$$F \equiv a_{11}x^2 + 2a_{12}xy + \frac{a_{12}^2}{a_{11}}y^2 + 2a_{13}x + 2a_{23}y = 0$$

or

$$(a_{11}x + a_{12}y)^2 + 2a_{11}(a_{13}x + a_{23}y) = 0$$

passes by the substitution

$$\left. \begin{aligned} a_{11}x + a_{12}y &= 2a_{11}\xi \\ a_{13}x + a_{23}y &= -2a_{11}\eta \end{aligned} \right\} \dots \dots \dots (91)$$

into

$$\eta = \xi^2,$$

a solution of which (see 2nd comm. p. 590) is

$$\xi = e^{-\frac{\tau}{\sqrt{2}}}, \quad \eta = e^{-\tau\sqrt{2}} \dots \dots \dots (92)$$

Out of (91) and (92) we deduce

$$\left. \begin{aligned} x &= -\frac{2a_{11}}{A_{12}} \left(a_{23} e^{-\frac{\tau}{\sqrt{2}}} + a_{13} e^{-\tau\sqrt{2}} \right) \\ y &= \frac{2a_{11}}{A_{12}} \left(a_{13} e^{-\frac{\tau}{\sqrt{2}}} + a_{11} e^{-\tau\sqrt{2}} \right) \end{aligned} \right\} \dots \dots \dots (93)$$

These formulae are always applicable, as the supposition $A_{12} = 0$ would imply the degeneration of the parabola.

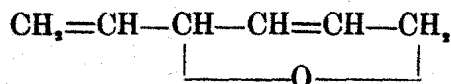
Chemistry. — “*On some internal unsaturated ethers*”. By J. W. LE HEUX. (communicated by Prof. VAN ROMBURGH).

(Preliminary communication).

(Communicated in the meeting of April 26, 1912).

By the action of formic acid on mannitol FAUCONNIER obtained a mixture of formic esters of this hexavalent alcohol, which submitted to dry distillation, yielded among other products a liquid of the composition C_6H_8O , boiling at 107° — 109° .

VAN MAANEN (Dissertation, Utrecht 1909) who investigated this substance and mentions it as a liquid boiling at 107° proposed as the most probable structural formula:



As the mode of formation of this substance does not give a complete insight into its structural formula, Prof. VAN ROMBURGH proposed to me to prepare the various possible oxides of hexadiene by other

methods which show more satisfactorily the progressive change of the reactions, and thus to find out the real structure of the substance prepared by FAUCONNIER.

As starting material was used the doubly unsaturated glycol $\text{CH}_2=\text{CH}-\text{CHOH}-\text{CHOH}-\text{CH}=\text{CH}_2$, which GRINER prepared by reduction of acrylaldehyde, divinylglycol.

Advantage was taken of the property of acetyl chloride to act on divalent alcohols in such a manner, that of the two alcohol-groups the one is converted into the hydrochloric, the other into the acetic ester.

The reaction product of acetyl chloride on divinylglycol is obtained as a colourless liquid, which after repeated fractionation under a pressure of 18 mM. boils at $84^\circ-88^\circ$. I have not yet obtained it in a perfectly pure state as the chlorine content was found a little too high. On keeping, the liquid darkens after a few days and then shows an acid reaction.

In order to prepare the oxide from the chloroacetine it was shaken for some time with strong aqueous sodium hydroxide and then distilled under reduced pressure (to prevent as much as possible, polymerisation). Of the distillate, which consists of two layers, the upper one is again distilled a few times over sodium hydroxide and finally over finely divided calcium in an atmosphere of hydrogen in order to obtain the product completely free from halogen and water.

The so prepared divinylethylene oxide



is a very mobile, colourless liquid, boiling at the ordinary pressure at $108^\circ-109^\circ$, with a very pungent odour characteristic of allyl compounds.

$$n_D^{15^\circ} = 1,44942. \quad d_{15} = 0,8834.$$

Once obtained in a pure state the oxide is permanent and only turns pale yellow on long keeping; under the influence of alkalis it resinifies when in contact with the air. When brought into contact with hydrogen chloride, this is absorbed immediately; on warming with water, divinylglycol is regenerated.

The ring $\text{—}\underset{\text{O}}{\text{C}-\text{C}}\text{—}$ is also opened comparatively easily by

amines.

For, if divinylethylene is heated with allylamine for a few hours

a compound is formed of 1 mol. of oxide and 1 mol. allylamine. By distillation and recrystallisation from petroleum ether, I obtained white needles melting at $37,5^{\circ}$. The oxide when heated with ammonia also gave a crystallised amino-alcohol.

Another method often applied to arrive at internal ethers consists in addition of hypochlorous acid to an unsaturated hydrocarbon and subsequent elimination of hydrogen chloride from the chlorhydrine formed. Before applying this method to hexatriene which might yield an oxide of the formula C_6H_8O , I first tried the action of this acid on a hydrocarbon with only one conjugated system of double bonds.

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \text{1.} \quad \text{2.} \quad \text{3.} \quad \text{4.} \end{array}$$

The hydrocarbon $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$, isoprene, which is now

readily prepared in a pure condition by means of the so-called HARRIES isoprene lamp, was cooled in ice-water and shaken in the dark with a solution of hypochlorous acid in such proportion that 1 mol. of acid was used for 1 mol. of isoprene.

The hypochlorous acid disappears spontaneously and the isoprene dissolves. After saturation of the liquid with common salt, ether extracts from this solution a compound boiling at $142^{\circ}-145^{\circ}$, the chlorine content of which points to its having the composition C_5H_8OCl . By removing from this compound hydrogen chloride by means of strong aqueous potassium hydroxide, I obtained a liquid with an ethereal odour b.p. $80^{\circ}-82^{\circ}$ which, however, still contained a trace of halogen.

Brought into contact with hydrogen chloride the latter is at once absorbed; when dissolved in carbon tetrachloride, the substance decolorises, although slowly, a solution of bromine.

If now we consider to which position in the isoprene molecule the HOCl can be attached the three following possibilities may occur.

1. The hypochlorous acid is attached to the double bond 1=2.
2. The hypochlorous acid is attached to the double bond 3=4.
3. or, because the two double bonds are in conjunction, the linking has taken place at the carbon atoms 1 and 4 with the appearance of a new double bond between the carbon atoms 2 and 3. In the latter case a 5-ring would, probably, have been produced from the chlorhydrine thus formed, namely a methylidihydrofurane. The ready absorption of hydrogen chloride does not, however, support the latter view.

I hope to be soon able to make further communication on this subject with which I am still occupied.

Utrecht, April 1912.

Org. Chem. Lab. University.

Chemistry. — “*The radioactivity of rubidium and potassium compounds.*” II. By Dr. E. H. BÜCHNER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of April 26, 1912).

Some time ago I described a series of experiments undertaken with the object of demonstrating the radioactivity of rubidium and eventually of other alkali metals by the photographic method¹⁾. I then only noticed an action on the sensitive plate with rubidium sulphate; the salts of other alkalis produced no effect. I have repeated these experiments and, as announced previously, I have inquired more in particular, whether the phenomenon might be attributable to a previous exposure of the salt to the light; in that case there can be no question of a real radioactivity, but we should have here an analogism of the wellknown experiments with calcium sulphide. According to NIEWENGLOWSKI, this substance acts on a photographic plate by means of rays which penetrate through aluminium, but only when it has been previously exposed to the light. In the present meaning of the word we cannot call calcium sulphide radioactive, because an external influence is at work; if the same happened with rubidium and potassium, these substances could neither be included among the radioactive ones. And because they differ in various respects from the other active substances, there is still some doubt left about this matter. It was, therefore, desirable to carry out some experiments in this direction.

For this purpose I have exposed, simultaneously, in one box, some photographic plates to the action of RbCl , RbNO_3 , and Rb_2SO_4 in the manner described previously, but of each salt two specimens were taken; one of these had been kept in complete darkness from 4 to 5 months, the other had been exposed to broad daylight for some days previous to the experiment. When developing after 90 days, no difference was found between the action of the two specimens, both having affected the plates in the same manner. Hence, it again becomes more probable that we are dealing here indeed with true radioactivity.

For the rest I have been able to confirm my previous results. Again, I have not succeeded in getting an action on the sensitive plate either with salts of potassium or with salts of caesium, sodium, and lithium, but on the other hand rubidium did affect the plate. With RbCl and RbNO_3 , also with Rb_2SO_4 , I found that the plate had

¹⁾ These Proc. 1909, p. 154.