

Citation:

Dorssen, W. van & Romburgh, P. van, The reduction of acraldehyde and some derivatives of s. divinyl glycol (3.4 dihydroxy 1.5 hexadiene). On the dimplest hydrocarbon with two conjugated systems of double bonds, 1.3.5 hexatriene, in:
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the three-phase line for solid iodine is intersected both on branch 1b and 1a and therefore the complication in the figure occurs at the side of the iodine.

Still greater complications may appear when according to Fig. 3 (previous communication) there exist liquids with a minimum pressure and when consequently the branches 1b, 1a and 1b can also appear at the side of the liquids richer in B, whose intersection at an equal pressure may coincide eventually with those of branch 2 or branch 3. When such systems have been more closely investigated it will not prove difficult to give detailed *t, x*-figures for the same.

Chemistry. — "*The reduction of acraldehyde and some derivatives of s. divinyl glycol (3.4 dihydroxy 1.5 hexadiene)*". By Prof. P. VAN ROMBURGH and W. VAN DORSEN.

(Communicated in the Meeting of November 25, 1905)

The reduction of acraldehyde (acroleïne) with sodium amalgam ¹⁾ as well as with zinc and hydrochloric acid ²⁾ has been studied by LINNEMANN, who states that he has obtained in the first case propyl and isopropyl alcohol, in the second case isopropyl and allyl alcohol, also a substance called acropinacone of the composition $C_6H_{10}O_2$, or rather a product of non-constant boiling point, of which the fractions boiling between 160°—170° and 170°—180° gave, on analysis, values which led to this formula.

CLAUS ³⁾ could not confirm the results of LINNEMANN as regards the formation of isopropyl alcohol in the reduction with zinc and hydrochloric acid.

GRINER ⁴⁾ has also repeated LINNEMANN's experiments with the object of preparing acropinacone (divinylglycol) but only obtained very small quantities of a liquid without constant boiling point which bore no resemblance to the glycol which, however, was obtained by him in fairly large quantity by reduction of acraldehyde in acetic acid solution with a copper-zinc couple. The other products of the reaction have not been further described by the author.

If we consider the formula of acraldehyde in connection with the

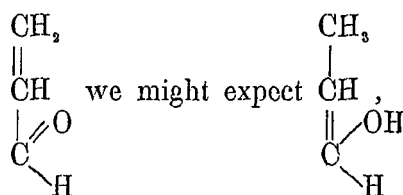
¹⁾ Ann. d. Chem. u. Pharm. 125 (1863) S. 315.

²⁾ Ibid Suppl. III (1864—1865) S. 257.

³⁾ B. B. III. (1870) S. 404.

⁴⁾ Ann. d. Phys. et Chim. [6] 26 (1892). p. 369.

views of THIELE on the addition of hydrogen to conjugated systems of unsaturated compounds, then on reducing



an unsaturated alcohol which, however, by intramolecular atomic shifting would be converted into $\text{CH}_3\text{—CH}_2\text{—C}\begin{smallmatrix} \text{O} \\ // \\ \text{H} \end{smallmatrix}$, propylaldehyde.

On further reduction this would form propyl alcohol, a substance which actually occurs among the products of the reduction.

Up to the present, propylaldehyde has not been found among the substances formed in the reduction of acraldehyde.

We have, however, succeeded in showing that, although no free propylaldehyde may be present, a derivative of this substance is formed under certain conditions so that the intermediate formation of the said aldehyde is not at all improbable.

First of all the reduction with zinc and hydrochloric acid in ethereal solution according to LINNEMANN has been studied, but we succeeded no more than GRINER in isolating a well defined product — besides allyl alcohol, and perhaps smaller quantities of propyl alcohol; generally, the substance obtained, which boiled between $158^\circ\text{—}164^\circ$, contained much chlorine.

If, however, we allow zinc dust to act on a mixture of acraldehyde and glacial acetic acid ¹⁾ then, in addition to allyl and propyl alcohol, a neutral liquid is formed (b.p. 170°) from which, after fractionating in vacuo, a product may be obtained boiling between $59^\circ\text{5'—}60^\circ$ at 15 mm. The analysis and the vapour density lead to the formula $\text{C}_9\text{H}_{14}\text{O}_2$.

The compound is not decomposed by potassium hydroxide; neither sodium nor phosphorus pentachloride have any action; it cannot be benzoylated with benzoyl chloride and pyridine. This sufficiently proves the absence of OH groups.

The said properties, however, render it very probable that the substance is an ether. By dilute acids it is hydrolysed although but slowly. An aldehyde-like odour appears but, as the reaction proceeds, the mass becomes so dark with formation of brownish-black resinous

¹⁾ The action of various reducing agents on acraldehyde has been studied. The results will be published in due course.

products that we have not, as yet, succeeded in isolating well-defined compounds.

Bromine is readily absorbed by it and that in a quantity which points to the presence of two double bonds. If we work with a solution of carbon tetrachloride at a low temperature, but little hydrogen bromide is formed.

From a substance of the formula $C_8H_{14}O_2$, a great many isomers are, of course, possible. We cannot enter here into a description of the different experiments made in order to elucidate the structure of the product obtained, but we may state that we have finally succeeded by means of a synthesis, which leaves no doubt whatever.

If, on s-divinyl glycol which, thanks to the beautiful researches of GRINER, may be readily prepared, propylaldehyde is allowed to act for 6 days at 90° , a substance is obtained identical with the one described above.

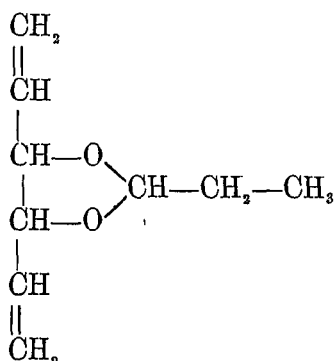
(Sp. gr. at 12° of the synthetic product 0.9392

" " " " " " original " 0.9416

Refraction at 12° of the synthetic " 1.4434

" " " " " " original " 1.4430.)

As to the synthetic product, propylidene s. divinylethylene ether, must be given the formula :



the original must also be considered as a derivative of propylaldehyde. It is, of course, possible that there might be formed at first an analogous acetaldehyde derivative, which afterwards got converted into a propylaldehyde derivative, but considering the comparative difficulty with which the vinyl group combines with hydrogen, this looks less probable.

As one of us (v. R.) explained many years ago, s. divinylglycol or 3.4 dihydroxy 1.5 hexadiene would form an excellent material for the preparation of the hydrocarbon $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$, otherwise hexatriene 1.3.5.

Different methods which we have tried have not led to the desired

end. At last we think we have succeeded by making use of the diformate of s-divinyl glycol, a compound which may be prepared by heating this glycol for a short time with formic acid.

By fractionating in vacuo, the diformate is obtained as a colourless liquid which at a pressure of 20 mm. boils at 109° and has a sp. gr. of 1.0747 at 11° . A determination of the formic acid (by saponification) gave the amount required for diformate.

In a communication about to follow, the hydrocarbon prepared from the diformate and the method of its preparation will be fully described.

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Chemistry. — “*The occurrence of β -amyrine acetate in some varieties of gutta percha*”. By Prof. P. VAN ROMBURGH and N. H. COHEN.
(Communicated in the meeting of November 25, 1905).

Last year, a compound melting at 234° was found by one of us (v. R.) in the gutta percha of *Payena Leerii*¹⁾ of which it could be stated that it is *not* identical with lupeol cinnamate, which occurs in many varieties of gutta percha; the quantity was then too small for further research. Since then a little more of that product was prepared so that it could be proved that on treatment with alcoholic potash it yields acetic acid and an alcohol melting at 195° .

In these Proc. of June 25, 1905 p. 137 it was stated that the same product has been found by one of us (C.) in the “djelutung” derived from the juice of varieties of *Dyera*. The identity was shown by a comparison of the melting points and by melting point determinations of mixtures of the two substances.

A sufficient quantity was now at disposal to determine the nature of the compound.

In the first place, the substance was recrystallised a few times and finally obtained in beautiful, long, hard needles which melted at 235° (corr. m. p. 240° — 241°).

On analysis (combustion with lead chromate) the following results were obtained:

		Calculated for $C_{32}H_{52}O_2$
C	81.96, 82.08.	C 82.06
H	11.24, 11.27.	H 11.11

The compound was found to be dextrorotatory. For the specific rotatory power in a chloroform solution $[\alpha]_D = 81^{\circ}.1$ was found.

As stated above, the substance melting at 235° when boiled with

¹⁾ B. B. 37 (1904) S. 3443.