

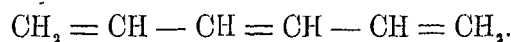
*Citation:*

Romburgh, P. van & Dorssen, W. van, On the simplest hydrocarbon with two conjugated systems of double bonds, 1.3.5. hexatriene, in:

KNAW, Proceedings, 8 II, 1905-1906, Amsterdam, 1906, pp. 565-568

**Chemistry.** — “*On the simplest hydrocarbon with two conjugated systems of double bonds, 1.3.5. hexatriene.*” By Prof. P. VAN ROMBURGH and W. VAN DORSSEN.

In 1878 TILDEN<sup>1)</sup> advanced the hypothesis that the terpenes might be derivatives of a hydrocarbon of the formula:



At the meeting of the Assoc. franç. pour l'avanc. des Sciences in Paris 28 Aug. 1878, FRANCHIMONT pronounced the same opinion and suggested that this compound might, perhaps, be obtained by eliminating of the two chlorine atoms from acrolein chloride. The efforts made by one of us (v. R.) many years ago to prepare that hydrocarbon in this manner did not prove successful. The researches on terpenes which afterwards definitely led to the result that, in the case of these substances, we are dealing with cyclic compounds made the above cited hydrocarbon recede into the background.

The views of THIMBLE on conjugated systems of double bonds, and the researches originated therefrom, in addition to the studies on the aliphatic terpenes myrcene and ocimene, hydrocarbons in which the existence of three double-bonds has been proved by different investigators, have again drawn our attention to the 1.3.5 hexatriene, because it would represent the simplest hydrocarbon in which occur three double linkings that also form two conjugated systems.

One of us (v. R.) has pointed out previously that one of the methods which might lead to the desired product consists in the action of metals on 3.4 dichloro-1.5 hexadiene.

The investigations of GRINER<sup>2)</sup> have acquainted us with the analogous bromine compound which is formed by the action of phosphorus tribromide on s. divinyl glycol. We have treated this substance, prepared according to GRINER's directions, with metals but have not yet succeeded in preparing the hydrocarbon in that way. There was however, another way still at our disposal to gain our object, namely, by starting from s. divinyl glycol and converting this into a formic ester.

It is known that the formates of polyhydric alcohols, in which occur a OH-group and a formic acid-residue connected with two C-atoms linked together, yield, on heating, unsaturated compounds with elimination of carbon dioxide and water. It was now obvious to prepare the monoformate of divinyl glycol. We endeavoured to do this by heating this glycol with oxalic acid but obtained, mainly, brownish

<sup>1)</sup> Journ. chem. Soc. 1878. p. 80.

<sup>2)</sup> Ann. d. Chim. et d. Phys. [6] 26 (1892) p. 305.

compounds not looking fit for further investigation. By cautious treatment with formic acid the diformate was, however, readily obtained (see p. 544).

In order to convert this into the hydrocarbon, a reaction was applied which one of us had previously used for preparing allyl alcohol from the diformate of glycerol, and which consists in heating that compound with glycerol.

And, indeed, a mixture of the diformate of divinyl glycol with the glycol when heated slowly, first at  $165^{\circ}$  and then gradually to  $200^{\circ}$ , evolves carbon dioxide and a little carbon monoxide and yields a distillate consisting of two layers, the upper one of which consists of a hydrocarbon.

The triformate of glycerol, like the diformate of divinyl glycol, may be distilled without notable decomposition by heating it somewhat rapidly at the ordinary pressure. Recently one of us (v. R.) found however that it is decomposed by prolonged heating at a temperature a little below the boiling point and it then yields the same decomposition products as the diformate of glycerol.

If now the diformate of s. divinyl glycol is heated at  $165^{\circ}$  and the temperature allowed to rise very slowly, an evolution of gas is observed and in the receiver is collected a liquid consisting of two layers. The upper layer again consists of a hydrocarbon identical with the one cited above.

Probably, the simplest way to explain this reaction is to assume that the diformate contains a little monoformate which is decomposed in the desired sense, with formation of water which in turn regenerates monoformate from the diformate. Finally, a residue consisting of glycol (respectively, polyglycols) is obtained and in the distillate a little formic acid is found, besides water, whilst the gases evolved consist of carbon dioxide and carbon monoxide. The last method appears to give a better yield than the first one.

The hydrocarbon formed is separated and distilled, the portion distilling up to  $95^{\circ}$  being collected. It is then dried over a piece of caustic potash, which also removes traces of formic acid and then rectified a few times over metallic sodium.

It then forms a colourless, strongly refractive liquid with a slight pungent odour; in contact with the air it appears to slowly oxidise. The boiling point lies between  $77^{\circ}$ — $82^{\circ}$ , the main fraction boils between  $78^{\circ},5$ — $80^{\circ}$  (corr.; pressure 766 m.m.)

The analysis and the vapour density gave values leading to the composition  $C_6 H_8$ .

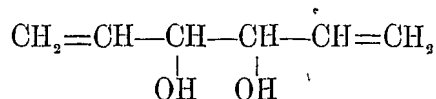
For the physical constants of the main fraction was found :

Spec. gr.<sub>10</sub> 0,7565 $n_{D10}$  1.49856.

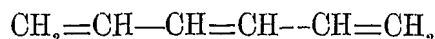
If we calculate the molecular refraction from these data, with the aid of the formula of LORENTZ—LORENZ, we find  $MR = 31,03$ , whilst for  $C_6H_8$  is found  $MR = 28,53$  assuming that the hydrocarbon possesses three double bonds, and making use of the atomic refractions of CONRADY<sup>1)</sup> and the increment for the double bond.

The difference of 2,5 between the calculated and found molecular refraction is a striking one. According to BRÜHL<sup>2)</sup> excesses always occur with substances with a conjugated system of double bonds. In the aliphatic terpene ocimene, an excess (to the extent of 1.76) is also found, and this assumes an extraordinarily large proportion in the case of allo-ocimene.<sup>3)</sup>

As regards the structural formula of the hydrocarbon obtained, its formation from

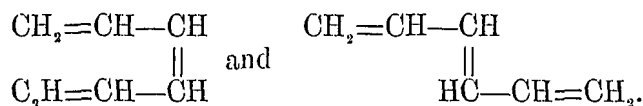


by the elimination of the two OH-groups by means of formic acid points to the formula:

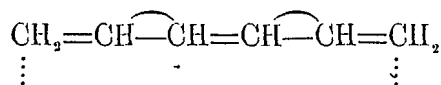


which indeed represents 1.3.5-hexatriene.

A glance at this formula shows that it may appear in two geometrical isomeric forms, namely in the *cis* and *trans* form<sup>4)</sup>:



If, with THIELE<sup>5)</sup>, we accept partial valencies the formula of 1.3.5-hexatriene should be written:



Unsaturated hydrocarbons with a conjugated system readily take

1) Zeitschr. physik. Chem. 3, 226.

2) B.B. 38, 768.

3) C. J. ENKLAAR, Dissertation 1905. Compare literature on the subject p. 87.

4) Probably, the hydrocarbon is a mixture of both. In the fractionation, besides the main fraction, a distillate could be obtained boiling between 77.5° and 78° 5 (sp. gr.<sub>10</sub> 0.7558,  $n_{D10}$  1.494  $MR$  30.8), also a final fraction boiling between 80°—82° (sp. gr.<sub>10</sub> 0.7584,  $n_{D10}$  1.503,  $MR$  31.2). We hope to repeat the experiment on a larger scale.

5) Ann. 306. 94.

up hydrogen on treatment with absolute alcohol and metallic sodium. In the reduction of our own hydrocarbon, 2,4 hexadiene might be expected in the first place, although, a priori the formation of other hexadienes is not to be excluded. In the 2,4 hexadiene



we have again, however a compound with a conjugated system which might be further hydrogenated to hexene 3.

In fact, our hydrocarbon when treated with boiling absolute alcohol and metallic sodium takes up hydrogen. The study of the product (or products) of the reaction is not facilitated by the contradictory statements found in the literature about the hexadienes. A future communication will treat more extensively of this reaction and also of the original hydrocarbon whose structure we will try to determine also by other methods. We may state further that a dibromine addition compound has been prepared melting at 89—90° and a tetra-compound melting at 115°.

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**Chemistry.** — “*On the hidden equilibria in the  $p,x$ -sections below the eutectic point*”. By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEMBOOM).

The  $p,x$ -sections of binary systems in the neighbourhood of the eutectic point have been fully discussed by BAKHUIS ROOZEMBOOM<sup>1)</sup>; in this the course of the solubility isotherms in the unstable and metastable region were, however, not examined. This problem could only be taken in hand after VAN DER WAAALS' paper<sup>2)</sup> on: “*The equilibrium between a solid body and a fluid phase, especially in the neighbourhood of the critical state*” had been published.

Availing myself of this paper I shall discuss the just-mentioned problem, and show briefly in what way the stable region is connected with the metastable and unstable region.

If for the two substances  $A$  and  $B$  the volume in solid state is larger than in liquid state, these substances will have negative melting-point curves, i. e.  $\frac{dp}{dt}$  will be negative, and the melting-point curve will therefore pass to lower temperatures with increase of pressure. If

<sup>1)</sup> Die Heterogene Gleichgewichte 2, 139 (1904).

<sup>2)</sup> These Proceedings Oct. 31, 1903, 439.