

Citation:

Dorssen, W. van & Romburgh, P. van, On some derivatives of 1-3-5-hexatriene, in:
KNAW, Proceedings, 9 I, 1906, Amsterdam, 1906, pp. 111-115

with diformin, however, cannot be distilled under those circumstances, but is decomposed with evolution of carbon monoxide and dioxide and formation of allyl formate.

If triformin is heated slowly a decided evolution of gas is noticed at 210° but in order to prolong this, the temperature must rise gradually. The gas evolved consists of about equal volumes of carbon monoxide and dioxide. The distillate contains as chief product allyl formate, some formic acid, and further, small quantities of allyl alcohol. In the flask a little glycerol is left ¹⁾.

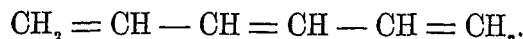
Triformin is but slowly saponified in the cold by water in which it is insoluble, but on warming saponification takes place rapidly.

Ammonia acts with formation of glycerol and formamide. With amines, substituted formamides are formed, which fact I communicated previously ²⁾.

The properties described show that triformin, the simplest fat, differs considerably in its properties from the triglycerol esters of the higher fatty acids.

Chemistry. — "*On some derivatives of 1-3-5-hexatriene*". By Prof. P. VAN ROMBURGH and Mr. W. VAN DORSEN.

In the meeting of Dec. 30 1905 it was communicated that, by heating the diformate of s-divinylglycol we had succeeded, in preparing a hydrocarbon of the composition C_6H_8 to which we gave the formula:



Since then, this hydrocarbon has been prepared in a somewhat larger quantity, and after repeated distillation over metallic sodium, 50 grams could be fractionated in a LADENBURG flask in an atmosphere of carbon dioxide.

The main portion now boiled between 77°—78°.5 (corr.; pressure 764.4 mm.).

Sp. gr. _{13.5}	0.749
$n_{D13.5}$	1.4884

Again, a small quantity of a product with a higher sp. gr. and a larger index of refraction could be isolated.

¹⁾ This decomposition of triformin has induced me to study the behaviour of the formates of different glycols and polyhydric alcohols on heating. Investigations have been in progress for some time in my laboratory.

²⁾ Meeting 30 Sept. 1905.

In the first place the action of bromine on the hydrocarbon was studied.

If to the hydrocarbon previously diluted with chloroform we add drop by drop, while agitating vigorously with a WITT stirrer, a solution of bromine in the same solvent, the temperature being -10° , the bromine is absorbed instantly and as soon as one molecule has been taken up the liquid turns yellow when more is added. If at that point the addition of bromine is stopped and the chloroform distilled off in vacuo, a crystalline product is left saturated with an oily substance. By subjecting it to pressure and by recrystallisation from petroleum ether of low boiling point, fine colourless crystals are obtained which melt sharply at $85^{\circ}.5-86^{\circ} 1)$.

A bromine determination according to LIEBIG gave 66.84%, $C_6H_8Br_2$ requiring 66.65%.

A second bromine additive product, namely, a tetrabromide was obtained by the action of bromine in chloroform solution at 0° in sunlight; towards the end, the bromine is but slowly absorbed. The chloroform is removed by distillation in vacuo and the product formed is recrystallised from methyl alcohol. The melting point lies at $114^{\circ}-115^{\circ}$ and does not alter by recrystallisation. Analysis showed that four atoms of bromine had been absorbed.

Found: Br: 80.20. Calculated for $C_6H_8Br_4$ 79.99.

A third bromine additive product was found for the first time in the bromine which had been used in the preparation of the hydrocarbon to retain any hexatriene carried over by the escaping gases. Afterwards it was prepared by adding 3 mols of bromine to the hydrocarbon diluted with 1 vol. of chloroform at 0° and then heating the mixture at 60° for 8 hours. The reaction is then not quite completed and a mixture is obtained of tetra- and hexabromide from which the latter can be obtained, by means of ethyl acetate, as a substance melting at $163^{\circ}.5-164^{\circ}$.

Found: Br. 85.76. Calculated for $C_6H_8Br_6$ 85.71.

On closer investigation, the dibromide appeared to be identical with a bromide obtained by GRINER¹⁾ from s. divinyl glycol with phosphorus tribromide; of which he gives the melting point as $84^{\circ}.5-85^{\circ}$. A product prepared according to GRINER melted at $85^{\circ}.5-86^{\circ}$ and caused no lowering of the meltingpoint when added to the dibromide of the hydrocarbon.

GRINER obtained, by addition of bromine to the dibromide prepared from his glycol, a tetrabromide melting at 112° together with a

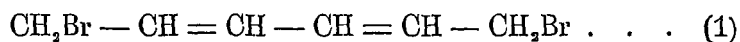
¹⁾ Not at 89° as stated erroneously in the previous communication.

product melting at 108°—109°, which he considers to be a geometrical isomer. On preparing ²⁾ the tetrabromide according to GRINER the sole product obtained was that melting at 112°, which proved identical with the tetrabromine additive product prepared from the hydrocarbon, as described above. For a mixture of these two bromides exhibited the same meltingpoint as the two substances separately.

Prolonged action of bromine on the tetrabromide according to GRINER, yielded, finally, the hexabromide melting at 163°—164°, which is identical with the one prepared from the hydrocarbon.

The bromine derivatives described coupled with the results of GRINER prove that our hydrocarbon has indeed the formula given above.

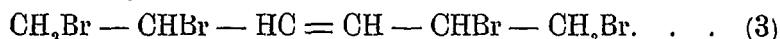
According to THIELE's views on conjugated double bonds we might have expected from the addition of two atoms of bromine to our hexatriene the formation of a substance with the formula



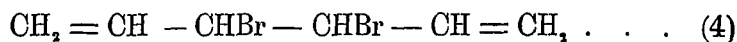
or



from the first of which, on subsequent addition of two bromine atoms the following tetrabromide would be formed.



As, however, the dibromide obtained is identical with that prepared from *s. divinyl glycol*, to which, on account of its mode of formation, we must attribute the formula



(unless, what seems not improbable considering certain facts observed, a bromide of the formula (1) or (2) should have really formed by an intramolecular displacement of atoms) the rule of THIELE would not apply in this case of two conjugated systems.

Experiments to regenerate the glycol from the dibromide have not as yet led to satisfactory results, so that the last word in this matter has not yet been said. The investigation, however, is being continued.

Meanwhile, it seems remarkable that only the first molecule of bromine is readily absorbed by a substance like this hexatriene, which contains the double bond three times.

By means of the method of SABATIER and SENDERENS, hexatriene may be readily made to combine with 6 atoms of hydrogen. If its

¹⁾ Ann. chim. phys. [6] 26. (1892) 381.

²⁾ Investigations on a larger scale will have to decide whether an isomer, melting at 108°, really occurs there as a byproduct which then exerts but a very slight influence on the melting point of the other product.

vapour mixed with hydrogen is passed at 125°—130° over nickel reduced to a low temperature, the hydrogen is eagerly absorbed and a product with a lower boiling point is obtained, which, however, contains small quantities of unsaturated compounds (perhaps also cyclic ones). In order to remove these, the product was treated with bromine and after removal of the excess and further purification it was fractionated. As a main fraction, there was obtained a liquid boiling at 68°.5—69°.5 at 759.7 mm.

$$Sp. gr._{12} = 0.6907 \quad n_{D_{12}} = 1.3919.$$

Although the boiling point agrees with that of the expected hexane the sp. gr. and the refraction differ still too much from the values found for hexane by BRUHL and by EYKMAN¹⁾.

Therefore, the product obtained from hexatriene was shaken for some time with fresh portions of fuming sulphuric acid until this was no longer coloured. After this treatment were obtained one fraction of

B. p. 69°—70°, $Sp. gr._{14}$ 0.6718 $n_{D_{14}}$ 1.38250.
and another of

B. p. 69°.7—70°.5, $Sp. gr._{14}$ 0.6720, $n_{D_{14}}$ 1.38239.

An *n*-hexane prepared in the laboratory, according to BRUHL²⁾ by Mr. SCHERINGA gave the following values

B. p. 69°, $Sp. gr._{14}$ 0.664 $n_{D_{14}}$ 1.3792

whilst an *n*-hexane prepared, from diallyl according to SABATIER and SENDERENS, by Mr. SINNIGE gave

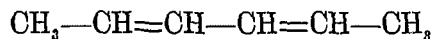
B. p. 68.5°—70°, $Sp. gr._{10}$ 0.6716, $n_{D_{10}}$ 1.38211.

It is, therefore, evident that the hexane obtained by SABATIER's, and SENDERENS' process still contains very small traces of impurities.

There cannot, however, exist any doubt that 1-3-5-hexatriene absorbs 6 atoms of hydrogen with formation of normal hexane.

Of greater importance, however, for the knowledge of the new hydrocarbon is the reduction by means of sodium and absolute alcohol.

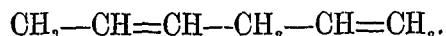
If, as a rule, unsaturated hydrocarbons are not likely to take up hydrogen under these circumstances, it becomes a different matter when a conjugated system is present. Now, in 1-3-5-hexatriene, two conjugated systems are found and we might therefore expect the occurrence of a 2-4-hexadiene:



¹⁾ BRUHL (B. B. 27, (1894) 1066) finds $Sp. gr._{20} = 0.6603$, $n_{D_{20}} = 1.3734$; EYKMAN (R. 14, (1881) 187) $Sp. gr._{14} = 0.6652$ $n_{D_{14}} = 1.37725$.

²⁾ Ann. 200, 183.

or, of a 2-5-hexadiene :



The first, still having a conjugated system can again absorb two atoms of hydrogen and then yield hexene 3.



whilst the other one cannot be hydrogenated any further ¹⁾.

The results obtained seem to point out that both reactions have indeed taken place simultaneously, and that the final product of the hydrogenation is a mixture of hexadiene with hexene.

10 grams of 1-3-5-hexatriene were treated with 100 grams of boiling absolute alcohol and 15 grams of metallic sodium. After the sodium had dissolved, a current of steam was passed, which caused the ready separation of the hydrocarbon formed, which, however, still contained some alcohol. After redistillation, the hydrocarbon was washed with water, dried over calcium chloride and distilled over metallic sodium.

At 75°.5 it commenced to boil and the temperature then slowly rose to 81°. The liquid was collected in two fractions.

fraction I. B.p. 75°.5—78°, *Sp.gr.*₁₀ 0.7326 *n*_{D10} = 1.4532

„ II. „ 78° —79°.5. „ — „ = 1.4665

These fractions were again united and once more treated with sodium and alcohol. But after purification and drying no liquid of constant boiling point was obtained, for it now commenced to boil at 72°.5, the temperature rising to 80°. The main fraction now possessed the following constants:

B.p. 72°.5—74°, *Sp.gr.*₁₂ 0.7146 *n*_{D12} 1.4205

The fraction 75°—80 gave *n*_{D12} 1.4351.

An elementary analysis of the fraction boiling at 72°.5—74° gave the following result:

Found	Calculated for C ₆ H ₁₀	Calculated for C ₆ H ₁₂
C 87.06	87.7	85.6
H 13.32	12.3	14.4

The fraction investigated consists, therefore, probably of a mixture of C₆H₁₀ and C₆H₁₂. The quantity collected was insufficient to effect another separation. We hope to be able to repeat these experiments on a larger scale as soon as we shall have again at our disposal a liberal supply of the very costly primary material.

Utrecht, Org. Chem. Lab. University.

¹⁾ If CH₂=CH—CH₂—CH₂—CH=CH₂ should be formed, this will not readily absorb more hydrogen either.