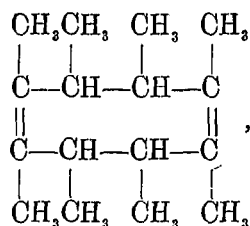
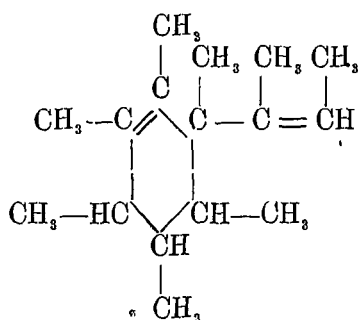


Citation:

Romburgh, P. van & Muller, P., 1: 3: 5 Hexatrienee, in:
KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 1090-1093



or in connexion with the researches of LEBEDEV¹⁾ on polymeric hydrocarbons, like



In order to elucidate the structure we have already made a great many experiments which, however, have not yet led to definite results.

If the hydrocarbon is treated with bromine there always takes place, besides the addition, an evolution of hydrogen bromide even in very strong dilution and cooling to -40° , and we did not succeed in isolating a well-defined compound. An effort was made to reduce the dimeride with sodium and alcohol, but it did not take up any hydrogen under those conditions. Reduction with hydrogen under the influence of platinum or palladium was also applied by us in vain, up to the present.

Oxidation with potassium permanganate has also failed to lead to positive conclusions. Experiments intended to attain the desired result with ozone are in progress.

Utrecht.

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Chemistry. — “1 : 3 · 5 *Hexatriene*.” By Prof. P. VAN ROMBURGH and Dr. P. MULLER.

(Communicated in the meeting of March 28, 1914).

One of us (v. R.) prepared in 1905, with Mr. VAN DORSSSEN, the above hydrocarbon by heating the formate of *s*-divinylglycol.

From this could be obtained by addition of bromine:

1. a dibromide $\text{C}_6\text{H}_8\text{Br}_2$ that proved identical with the *s*-divinyl-ethylene bromide prepared by GRINER.²⁾

¹⁾ Journ. Chem. Soc. 104 Abstr. 1285, (1913).

²⁾ Ann. d. Chimie et de phys. (6) 26, 367 (1892).

2. a tetrabromide $C_6H_8Br_4$, also already described by GRINER of the formula $CH_2=CH-CHBr-CHBr-CHBr-CH_2Br$.

3. a hexabromide $C_6H_8Br_6$, having the formula of a 1:2 3·4·5:6 hexabromohexane.

Addition of 6 atoms of hydrogen by the SABATIER and SENDERENS method gave normal hexane.

Although it was thus shown with certainty that by the process employed the desired unsaturated hydrocarbon was obtained, there remained some doubt as to its absolute purity, for instance, because the physical constants of the different preparations did not quite agree. It was, therefore, desirable to make efforts to get at a method that could yield this compound, so important from a theoretical point of view, in a perfectly pure condition. After many tedious experiments we have at last succeeded.

First of all we tried to gain our object by modifications in the old method; after many experiments the following *modus operandi* was found to give the best results.

s-divinylglycol is heated with an equal weight of 99% formic acid for half an hour at 105° , the excess of acid is then distilled off in vacuo at 60° and the mixture of formates is decomposed rapidly by heating at the ordinary pressure at 160° — 220° . The upper layer of the distillate is washed with water and distilled in an atmosphere of carbon dioxide or hydrogen, so as to avoid oxidation, up to 110° and the liquid obtained is dried over fused calcium chloride. Owing to the modifications introduced the yield of hydrocarbon is considerably larger and amounts to 40% of the glycol used.

A careful fractionate distillation of the hydrocarbon obtained did not, however, give even now a product with a constant boiling and melting point.

Experiments made to purify the preparation by freezing, although rising the initial fusion range¹⁾ could not be continued as the quantity at disposal was not sufficient. Hence, another method of preparing had to be looked for.

It was to be expected that by the action of dehydrating agents on hexadiene 1.5-ol 1.4 the desired hydrocarbon might form. This alcohol, obtained by Mr. LE HEUX²⁾ according to FOURNIER's method, was treated with potassium pyrosulphate or phthalic anhydride. From 80 grams of the alcohol could be obtained by heating with 5—10 grams of potassium pyrosulphate 24 grams, and by heating

¹⁾ The initial fusion trajectory was -55° to $-47^\circ.5$, the final $-47^\circ.5$ to -33° .

²⁾ This Proceedings, Febr. 1913, p. 1184.

with the theoretical quantity of phthalic anhydride 30 grams of a product boiling below 100° , which, however, on continued purification, yielded the same amount of hexatriene. The boiling point ($80^{\circ}.3-82^{\circ}$) as well as the melting point ($-34^{\circ}.5$ to -29°) was higher than that of the hydrocarbon prepared by the first method; a pure product could, however, not be obtained from the quantity at disposal.

Hence, we had recourse to the preparation from a crystallized substance namely from the above mentioned dibromide $C_6H_8Br_2$ prepared, according to GRINER, by the action of phosphorus tribromide on s-divinylglycol. The bromide purified by recrystallisation gives, on treating the boiling alcoholic solution with zinc dust, a good yield of pure hexatriene. This was placed over fused calcium chloride so as to remove water and alcohol. After fractionating in an atmosphere of carbon dioxide or hydrogen a liquid was obtained (b.p. $80^{\circ}.5-82^{\circ}$ at 765 m.m.) which solidified in a mixture of ice and salt and melted at $-11^{\circ}.5$ to $-9^{\circ}.5$. $d_4^{16.7} = 0.7355$. $n_D^{16.7} = 1.5150$.

$$MR_D = 32.82. \text{ Calculated for } C_6H_8\bar{3} = 28.5.$$

For the specific exaltations were found:

$$E_{\Sigma\alpha} = 5.11$$

$$E_{\Sigma D} = 5.39$$

$$E_{\Sigma\beta} - E_{\Sigma\alpha} = 1.26 = 136.5\%$$

$$E_{\Sigma\gamma} - E_{\Sigma\alpha} = 2.23 = 152\%$$

As will be noticed, the specific exaltations of the refraction reach a remarkably high figure.

If we allow bromine to act on a solution of the pure hexatriene in carbon tetrachloride or carbon disulphide, s-divinylethylenebromide, m.p. 87° , is obtained quantitatively.

Hexatriene gets readily polymerised, particularly on warming. As in the above mentioned preparation of the hydrocarbon a fractional distillation at the ordinary pressure was applied for the purpose of purification, there was a chance that in this operation the distillate also might be contaminated with the polymeride.

Therefore, a new supply was prepared which was dried, first over calcium chloride and then over potassium hydroxide¹⁾; it then exhibited the following constants: m.p. -11° ; b.p. $80^{\circ}-80^{\circ}.5$ (at 755 mm.) $d_4^{12.5} = 0.7432$. $n_D^{12.5} = 1.5183$; $MR_D = 32.6$.

After a distillation in vacuo at which the hydrocarbon passed over

¹⁾ If the hydrocarbon is pure, the KOH remains uncoloured. If, however, it contains oxidation products, the latter turns brown at the surface.

at the temperature of the room and was cooled in a mixture of solid carbon dioxide and alcohol it gave the following results: m.p. $-10^{\circ}.5$; $d_4^{13.5} = 0.740$; $n_D^{13.5} = 1.5172$; $MR_D = 32.7$.

After standing for a week over potassium hydroxide this liquid was again distilled at the ordinary pressure. Now was found: m.p. -11° to -10° ; $d_4^{14} = 0.7396$; $n_D^{14} = 1.5167$; $MR_D = 32.7$.

From this we notice that the distillation at the ordinary pressure exerts no influence on the properties of the hydrocarbon so that the above-cited constants may be really taken to be those of pure hexatriene. The results mentioned here briefly, will be communicated more fully elsewhere.

Utrecht.

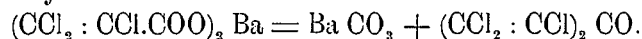
Org. Chem. Lab. University.

Chemistry. — “*On dichloroacetylene*”. (A warning). By Prof. J. BÖESEKEN and J. F. CARRIÈRE. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of March 28, 1914)

Our object was to prepare di-trichlorovinylketone from trichloroacrylic acid by elimination of carbon dioxide and water.

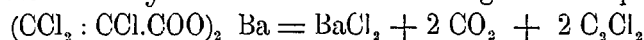
It was, therefore, first attempted to effect this decomposition by a careful dry distillation of the barium salt:



In a provisional investigation it appeared however, that a strong charring took place, whilst the barium was left in the form of chloride.

When the experiment was repeated much carbon dioxide was evolved and further a gas with a disgustingly sweet odour, which formed a strong nebula in contact with the air.

This nebula formation was coupled with a decided chemo-luminescent phenomenon, so that we suspected that the most simple carbon chloride *dichloroacetylene* had formed according to the equation.



As we had to take into account the possibility of dealing with a very explosive compound, a quantity of only one gram of the barium salt was slowly heated in a dry current of hydrogen. After first passing the gases through an empty suction tube, in which a fairly large quantity of bye-product (with high b.p.) was retained, they passed through a similar tube placed in a DEWAR vessel in which the temperature was brought to -70° .

In this remained a little of a colourless, solid substance which melted below -50° to a mobile, colourless drop of liquid.