

Citation:

Romburgh, P. van & Wensink, D.W., A new hydrocarbon from the pinacone of methylethylketone, in: KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 1088-1090

is reached, and passes therefore to the group for which $\epsilon > \nu h$, whereas another part emits all the stored energy. For the chance of emission we find another value than PLANCK. This is not astonishing as we assumed that for $\epsilon > \nu h$ the function of probability would be continuous, whereas according to PLANCK it exhibits new discontinuities at $\epsilon = 2\nu h$ etc. At all events we see that PLANCK's hypothesis concerning the zero-point energy can only be reconciled with the thermodynamic law of the equilibrium change, when the function of probability shows a discontinuity at $\epsilon = \nu h$, of entirely the same nature as had already been assumed by PLANCK.

In conclusion we will calculate I , as this quantity occurs in the formula for the equilibrium constant. Integration of (23a) with

$$U = \frac{\nu h}{e^{\frac{\theta}{\nu h}} - 1} + \frac{1}{2} \nu h \text{ yields:}$$

$$I = \frac{h e^{-\frac{1}{2} \frac{\nu h}{\theta}}}{1 - e^{-\frac{\nu h}{\theta}}}$$

This expression differs from the value which we found without zero-point energy, and which we shall call I' by the factor $e^{-\frac{1}{2} \frac{\nu h}{\theta}}$. Hence we may write (20b) in the following form:

$$K = e^{-\frac{\Delta \epsilon}{\theta}} e^{-\frac{1}{2} \sum \frac{\nu h}{\theta}} III'.$$

And Q_0 being $= (\Delta \epsilon + \sum \frac{1}{2} \nu h)$, we find the same expression as without zero point energy, since then $Q_0 = \Delta \epsilon$, and we may, therefore, always write.

$$K = e^{-\frac{Q_0}{\theta}} III'.$$

Chemistry. — “A new hydrocarbon from the pinacone of methyl-ethylketone”. By Prof. P. VAN ROMBURGH and Miss D. W. WENSINK.

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

When studying the action of formic acid on this pinacone this seemed to take a course quite contrary to expectation. Whereas in this reaction the ordinary pinacone is almost completely converted

into pinacolin, a considerable quantity of a hydrocarbon is obtained here in addition to a pinacolin. A formate of the pinacone could not be isolated.

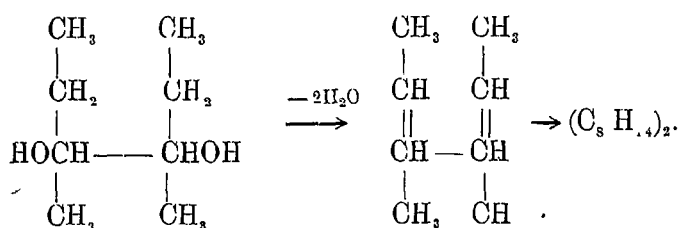
If we treat pinacone from methylethylketone with an equal weight of 97% formic acid, the liquid, particularly on warming, turns a beautiful red colour and after about a quarter of an hour's heating in a waterbath, the homogeneous mixture separates into two layers, the upper one of which is nearly colourless. The bottom layer which has a dark red colour gives, when diluted with water, a pale coloured supernatant layer. The united layers were washed with water and dried over potassium carbonate. On distilling at the ordinary pressure up to 150° a liquid was obtained which proved to consist mainly of the pinacolin $(\text{CH}_3)_2 \cdot \text{C}_2\text{H}_5 \cdot \text{C} \cdot \text{CO} \cdot \text{C}_2\text{H}_5$.

The residue was distilled in vacuo when as main product was obtained a pale yellow viscous liquid b. p. 130°. By fractionating over metallic sodium a colourless distillate with an agreeable odour was finally obtained. $d_4^{13.5} = 0.8741$, $n_D^{13.5} = 1.4864$. $\text{MR}_D = 72.3$ calculated for $\text{C}_{16}\text{H}_{28}$ \bar{M}_2 72.9.

The elementary analysis gave: C 86.96, 87.16; H 13.17, 12.82%. Calculated for $\text{C}_{16}\text{H}_{28}$: C 87.27, H 12.72%.

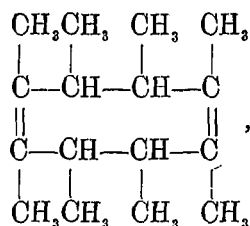
The determination of the molecular weight (by means of the lowering of the freezing point of benzene) gave 216.3 and 207; calculated for $\text{C}_{16}\text{H}_{28}$ 220.

HERSCHMANN¹⁾ found that by the action of concentrated sulphuric acid at 0° pinacolin occurs only, but on heating with 5% sulphuric acid was formed, besides pinacolin, also a hydrocarbon C_8H_{14} b. p. 117°—121°, which, as noticed by us, is converted on heating with formic acid into a dimeride identical with our hydrocarbon $\text{C}_{16}\text{H}_{28}$.

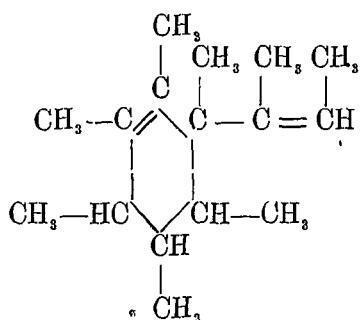


One might imagine the structure of the hydrocarbon $\text{C}_{16}\text{H}_{28}$ to be like that of an octomethylcyclo-octadiene:

¹⁾ Monatshefte 14, 233 (1893).



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.

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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).