22. The Structure of an Orange Colored Hydrocarbon, $C_{10}H_{10}$.

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The formation of orange colored hydrocarbon, $C_{10}H_{10}$, as a by-product during the synthesis of cyclooctatetraene by the polymerization of acetylene in the presence of nickel catalysts under pressure was reported by W. Reppe.¹⁾ We found that this hydrocarbon could be produced predominantly from acetylene and monovinylacetylene under the same condition as that of Reppe. This has led us to the study of its chemical structure.

In hydrogenation of $C_{10}H_{10}$ hydrocarbon with PtO_2 in glacial acetic acid, there was steady absorption of hydrogen, equivalent to four double bonds. Then hydrogen absorption dropped rapidly. After the absorption of hydrogen, equivalent to four double bonds, a colorless hydrocarbon, $C_{10}H_{18}$, was formed. Complete hydrogenation was attained by Raney-nickel catalyst under pressure at $150^\circ C$, and $C_{10}H_{20}$ hydrocarbon was formed.

$$\begin{array}{ccc}
 & C_{10}H_{10} & \\
 PtO_2 \swarrow & & \searrow R-Ni \\
 & 4H_2 & 5H_2 \text{ under press.} \\
 & \swarrow & \searrow 150^\circ C \\
 C_{10}H_{18} & & C_{10}H_{20}
 \end{array}$$

Table I. Physical constants of $C_{10}H_{16}$, $C_{10}C_{18}$, $C_{10}H_{20}$, and ethyl-cyclooctane.

Hydrocarbon	C ₁₀ H ₁₀	C ₁₀ H ₁₈	C ₁₀ H ₂₀	Ethyl- cyclooctane
Colour	orange	none	none	none
b.p.	92-93°/29 mm.	88-89°/31 mm.	81-82°/28 mm.	81-82°/27 mm.
d ₄ ²⁰	0.9295	0.8426	0.8381	0.8376
n _D ²⁰	1.5750	1.4741	1.4610	1.4620
MR _D calcd	43.9	45.7	46.2	46.2
found	46.2	45.8	46.1	46.0
Exaltation in MR _D	+2.3	+0.1	-0.1	-0.2

$C_{10}H_{18}$ hydrocarbon possessed one $C-CH_3$ as the result of the C-Methyl analysis. When its ozonide was oxidized by CrO_3 in acetic acid, suberic acid and η -oxocapric acid were obtained. As shown in Figure 1, these experimental results were thoroughly explained by the conclusion that the $C_{10}H_{18}$ hydrocarbon was 1-ethyl-cyclo-octene-(1).

$C_{10}H_{20}$ hydrocarbon, obtained by hydrogenation of $C_{10}H_{10}$ with Raney-nickel under pressure at 150° , was of saturated hydrocarbon possessing one $C-CH_3$. When it was oxidized by CrO_3 in acetic acid, suberic acid was obtained. According to results of these experiments, it was assumed that $C_{10}H_{20}$ was ethyl-cyclooctane as shown in Figure 2. This assumption was confirmed by the following fact that the physical constants of ethyl-cyclooctane, which was synthesized from brom-cyclooctane and ethyl iodide by Wurtz-Fittig reaction, were identical with that of $C_{10}H_{20}$ as shown in Table I.

Fig. 2. CrO_3 -oxidation of $C_{10}H_{20}$.Fig. 1. Ozone-oxidation of $C_{10}H_{16}$.

The orange yellow hydrocarbon, $C_{10}H_{10}$, has such physical constants as shown in Table I. It is noteworthy that remarkable exaltation in MR_D is present. Considering the facts that $C_{10}H_{18}$ was ethyl-cyclooctene and $C_{10}H_{20}$ was ethyl-cyclooctane, it was first assumed that $C_{10}H_{10}$ might be vinyl-cyclooctatetraene. But, from this hydrocarbon, formaldehyde could not be found in the products

Fig. 3. Possible structures of $C_{10}H_{10}$.

of ozonolysis, therefore there was no vinyl radical in $C_{10}H_{10}$. Moreover, there was no $C-CH_3$. Hence $C_{10}H_{10}$ might possess a ring structure having no side chain. Among the various possible ring structures, considering the Bredt's rule and possibility of formation of ethyl side chain by the hydrogenolysis, following two structures (a and b Fig. 3) might be possible. However, in consideration of what A.C. Cope²⁾ had reported about the formation of ethyl benzen or bicyclo-(4 2 0)-octan, although in a very small amount, as the by-product in the reduction of cyclooctatetraene under special conditions,

cyclodecapentaene (c in Fig. 3) could not also be excluded as the possible structure of $C_{10}H_{10}$.

In order to decide which structure is correct, some chemical experiments were carried out, but no conclusive result was obtained. Then we studied on the basis of physico-chemical experiments.

Refractive index: $C_{10}H_{10}$ possesses large exaltation in MR_D , a value of 23. In comparison with the exaltation exhibited by the various other ring compounds, the structure (a) is most probable as $C_{10}H_{10}$, because, in the structure (b) or (c), such large exaltation cannot be expected.

Magnetic susceptibility: The dia-magnetism for $C_{10}H_{10}$ was found to be 69.5×10 , and calculated values by Pascal were 68×10^{-6} , 68×10^{-6} , and 63×10^{-6} for the structure (a), (b) and (c), respectively. Therefore, on the basis of assumption that the resonance stabilization in $C_{10}H_{10}$ is so small as considered from its unstability, the structure (a) or (b) become probable.

Polarography: The polarography of $C_{10}H_{10}$ shows well defined waves in the presence of tetramethylammonium ions as that of cyclooctatetraene and the half wave potential is -1.408 volt vs. saturated calomel electrode in a 50% alcohol solution. According to Elofson³⁾, this polarographic evidence suggests an unusually highly polarized or polarizable double bond or conjugated double bond system, hence, either structure (a) or (c) is probable.

Although, we cannot give any conclusive structures from these experimental data, it seems safe to assume that the orange colored hydrocarbon, $C_{10}H_{10}$, is either bicyclo (0.2.6)-decatetraene-(2.4.6.9) (structure a) or cyclodecapentaene (structure c) having predominantly the structure (a) in resonance state.

We are now studying on further evidence for the structure of this substance. Details of this experiment will be reported elsewhere.

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References.

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