SYNTHESIS OF 2-CYCLOPENTYLOCTANE AND 5,5-DIMETHYLUDECANEO

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In the course of the development of methods for the investigation of ligroins in the N. D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR, various hydrocarbons were synthesized so as to provide standards for use in Raman-spectrum studies. The present paper describes the preparation of two hydrocarbons containing thirteen carbon atoms—a cyclopentane hydrocarbon with a branched side chain, 2-cyclopentyloctane, and a paraffin containing a tertiary carbon atom, 5,5-dimethylundecane. Neither of these hydrocarbons is described in the literature.

2-Cyclopentyloctane. The most convenient method of preparing monosubstituted cyclopentane homologs with a branched side chain is by hydrogenation of the corresponding fulvenes. This method has been used by several authors [1]. The best results on the hydrogenation of fulvenes (90-95% yield) were obtained by Kazansky and Terentyeva [2], who carried out the hydrogenation in the cold under a pressure of hydrogen in the presence of Raney nickel. It is by this method that we prepared 2-cyclopentyloctane, starting from 6-hexyl-6-methylfulvene, which was itself prepared by Thiele's method [3] by the condensation of 2-octanone with cyclopentadiene:

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} = \text{O} + \text{H}_2\text{C} \\
\text{n-C}_6\text{H}_{13} & \quad \text{CH} = \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{n-C}_6\text{H}_{13} & \quad \text{CH} = \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{n-C}_6\text{H}_{13} & \quad \text{CH} \quad \text{CH} \\
\text{H}_2\text{C}_8 & \quad \text{CH} \\
\text{CH}_2 & \quad \text{CH} \\
\text{n-C}_6\text{H}_{13} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{n-C}_6\text{H}_{13} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{n-C}_6\text{H}_{13} & \quad \text{CH} \quad \text{CH} \\
\text{H}_2 & \quad \text{C}_8 \\
\text{C}_8 & \quad \text{H}_2 \\
\text{C}_8 & \quad \text{H}_2 \\
\text{C}_8 & \quad \text{H}_2 \\
\text{C}_8 & \quad \text{H}_2 \\
\text{C}_8 & \quad \text{H}_2 \\
\end{align*}
\]

5,5-Dimethylundecane. This hydrocarbon was prepared from butylmagnesium bromide and 2-chloro-2-methylheptane in the presence of mercuric chloride. The necessary chloro compound was prepared from the corresponding alcohol, 2-methyl-2-octanol, which was synthesized by the Grignard reaction from hexylmagnesium bromide and acetone:

\[
\begin{align*}
n\text{-C}_6\text{H}_{13}\text{MgBr} + (\text{CH}_3)\text{C} & \rightarrow n\text{-C}_6\text{H}_{13}\text{C}(\text{CH}_3)\text{OH} \\
& \rightarrow n\text{-C}_6\text{H}_{13}\text{C}(\text{CH}_3)\text{Cl} \\
n\text{-C}_6\text{H}_{13}\text{MgBr} + n\text{-C}_6\text{H}_{13}\text{C}(\text{CH}_3)\text{Cl} & \rightarrow n\text{-C}_6\text{H}_{13}\text{C}(\text{CH}_3)\text{Cl} \quad \text{C}_8 \text{H}_{18-n}
\end{align*}
\]

EXPERIMENTAL

2-Octanone. This was purified through the bisulphite compound and had the following properties; b.p. 173.0° (760 mm); \(\text{n}^D_{20} 1.4156; \text{d}^2 0.8186\). The literature [4] gives: b.p. 172.6°-173.1° (752 mm); \(\text{n}^D_{20} 1.41613; \text{d}^2 0.8185\).

Cyclopentadiene. This was prepared by the depolymerization of its dimer, and it had the following properties; b.p. 39°-42°, \(\text{n}^D_{20} 1.4445\).
6-Hexyl-6-methylfulvene. A mixture of 178 g (1.39 moles) of 2-octanone and 100 g (1.51 moles) of cyclopentadiene was added dropwise at 10-14 °C to a solution of sodium ethoxide prepared from 33 g of sodium (1.43 moles) in absolute ethanol. The mixture was allowed to stand for one hour and then poured into cold water (1 liter). The upper layer was separated and washed with water to remove alkali. The fulvene, which was yellow in color, was distilled with superheated steam, separated from water, rapidly dried with calcium chloride, and vacuum-distilled; b.p. 94-96 °C (3 mm); yield 64.1 g (44.3%).

2-Cyclopentyloctane. Shortly after being distilled, the fulvene was loaded into a rotating autoclave and hydrogenated in ethanolic solution in the presence of Raney nickel at room temperature under an initial hydrogen pressure of 110 atmospheres. As soon as the pressure had fallen to fifty to sixty atmospheres, further hydrogen was pumped in. The hydrogenated hydrocarbon was steam-distilled, boiled with sodium, and repeatedly shaken with concentrated sulfuric acid and with sodium bisulfite solution. The 2-cyclopentyloctane was then passed through a silica-gel column and vacuum-distilled through a 40-plate column. The main distillate had the following properties: b.p. 236.0-236.5 °C (760 mm); 120.5 °C (19 mm); n_D^20 1.4475; d_4^20 0.8118; found MR 60.03; calculated for C_{12}H_{26} MR 60.03. The yield of 2-cyclopentyloctane was about 70%.

Hexyl Bromide. Reaction between 112 g (1.1 moles) of hexyl alcohol (b.p. 157.8-158.5 °C (760 mm); n_D^20 1.4180; d_4^20 0.8184), 480 g of 48% hydrobromic acid, and 68 ml of concentrated sulfuric acid gave 167 g of hexyl bromide b.p. 53.7-54.7 °C (20 mm); n_D^20 1.4472; d_4^20 1.1727. The literature [5] gives: b.p. 153.5 °C (760 mm); n_D^20 1.4478; d_4^20 1.1748.

2-Methyl-2-octanol. This tertiary alcohol was prepared by the Grignard reaction from hexylmagnesium bromide and acetone, which was first distilled through a 30-plate column. Three fractions from a Favorsky flask gave an 87.5% yield of 2-methyl-2-octanol, b.p. 91.0-91.5 °C (24 mm); n_D^20 1.4281; d_4^20 0.8239; found MR 45.04; calculated for C_9H_{20}O MR 45.29. The literature [6] gives: b.p. 82-85 °C (20 mm); n_D^20 1.427.

2-Chloro-2-methyloctane. 2-Methyl-2-octanol was saturated in the cold with gaseous hydrogen chloride until the increase in weight reached the necessary value. The yield was 88.8%; b.p. 66.4-67.1 °C (14 mm); n_D^20 1.4296; d_4^20 0.8566; found MR 49.01; calc. for C_{13}H_{26}Cl MR 48.63. This compound has not been described in the literature.

5,5-Dimethylundecane. A Grignard reagent was prepared from 264.3 g (1.73 moles) of butyl bromide and 46.93 g (1.93 g-atoms) of magnesium in ether; 10 g of mercuric chloride and then 157.5 g (0.97 mole) of 2-chloro-2-methyloctane were added at 20-22 °C. Toward the end of the addition there was noticeable evolution of gas and the mass thickened. After the usual treatment the ether was distilled off and the residue was heated with sodium to free it from mercury salts. After vacuum fractionation it was found that the head fraction contained 2-methyl-2-octene. 5,5-Dimethylundecane was freed from olefin impurities by chromatographic adsorption on silica gel and was then distilled through a 30-plate column. The main fraction had the following properties: b.p. 101.0 °C (16 mm); n_D^20 1.4272; d_4^20 0.7601; found MR 62.25; calc. for C_{13}H_{26} MR 62.23. The yield of pure product was 34 g, i.e., about 20% on the amount of 2-chloro-2-methyloctane taken.

SUMMARY

2-Cyclopentyloctane and 5,5-dimethylundecane were prepared for the first time. Their synthesis and properties are described.

LITERATURE CITED


