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Abstract

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ON THE INTERACTION OF TETRAMETHYLENE- AND PENTAMETHYLENEDIMAGNESIUM BROMIDES WITH Δ^2-CYCLOPENTENYL CHLORIDE

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In continuation of our studies (^{1}) on the preparation of hydrocarbons with two five-membered rings of the general formula

$$\text{[five-membered ring]—}(CH_2)_n\text{—[five-membered ring]}$$

for obtaining 1,4-dicyclopentylbutane and 1,5-dicyclopentylpentane, we have studied the interaction of Δ^2-cyclopentenyl chloride with the dimagnesium derivatives of 1,4-dibromobutane and 1,5-dibromopentane. According to the data of Braun (^{2}), in the case of each of these dibromides about 50% of the corresponding dimagnesium derivative is formed, together with dimagnesium derivatives of the condensation products of these dibromides, of the general formula $BrMg(CH_2)_nMgBr$, where $n = 8, 12$ or, respectively, $10, 15, 20$.

It turned out that the principal products of the reaction of Δ^2-cyclopentenyl chloride with tetramethylene- and pentamethylenedimagnesium bromide are the expected 1,4-di-(Δ^2-cyclopentenyl)butane (47-51%) or, respectively, 1,5-di-(Δ^2-cyclopentenyl)pentane (30%). However, together with hydrocarbons containing two five-membered rings, in both cases hydrocarbons containing one five-membered ring were also formed. The carbon skeleton of these hydrocarbons was proved by the fact that, upon their catalytic hydrogenation, respectively, *n*-butylcyclopentane and *n*-amylcyclopentane were obtained, the constants of which corresponded to the constants of these hydrocarbons reported in the literature (^{3}).

In the quantitative determination of the hydrogen added during hydrogenation of the unsaturated hydrocarbon with one five-membered ring, obtained by the interaction of Δ^2-cyclopentenyl chloride with pentamethylenedimagnesium bromide, it was shown that the molecule contains two double bonds. The position of these double bonds can be established on the basis of the structures of the starting substances: one bond, apparently, is located in the five-membered ring in position 2 relative to the substituent, while the second double bond was formed as a result of the elimination of one molecule of hydrogen halide.

The formation of olefins under the conditions of the Grignard reaction is characteristic of secondary and tertiary alkyl halides; however, this side reaction has also been observed in the case of primary alkyl halides. Thus, for example, Späth (^{4}) observed the formation of ethylene and octene in the interaction of ethylmagnesium bromide with secondary octyl bromide, the formation of amylene in the interaction of isoamylmagnesium bromide with isoamyl bromide, and also a number of other cases of olefin formation in Grignard reactions.

This double bond, apparently, must be in the α-position. Isomerization with migration of the double bond is hardly possible here, since

It is well known that the interaction of alkylmagnesium halides with allyl chloride or allyl bromide is one of the most reliable methods for obtaining α-olefins free from admixture of isomers with a different position of the double bond (^{5}). Thus, the hydrocarbons obtained in this way, each with one five-membered ring, may apparently be assigned the structures 1-(Δ^2-cyclopentenyl)but-3-ene and, respectively, 1-(Δ^2-cyclopentenyl)pent-4-ene.

Consequently, the results of the reactions between Δ^2-cyclopentenyl chloride and, respectively, tetramethylene- and pentamethylenedimagnesium bromide can be represented by the following schemes:

$$\text{BrMg(CH}_2)_4\text{MgBr}+\Delta^2\text{-cyclopentenyl chloride} \rightarrow 1,4\text{-di-}(\Delta^2\text{-cyclopentenyl})\text{butane}+1\text{-}(\Delta^2\text{-cyclopentenyl})\text{but-}$$

$$(47\text{–}51\%) \qquad (19\%)$$

$$\text{BrMg(CH}_2)_5\text{MgBr}+\Delta^2\text{-cyclopentenyl chloride} \rightarrow 1,5\text{-di-}(\Delta^2\text{-cyclopentenyl})\text{pentane}+1\text{-}(\Delta^2\text{-cyclopentenyl})\text{pen}$$

$$(30\%) \qquad (16\%)$$

1,4-Dicyclopentylbutane and 1,5-dicyclopentylpentane, previously unknown, were obtained by catalytic hydrogenation of 1,4-di-(Δ^2-cyclopentenyl)butane and, respectively, 1,5-di-(Δ^2-cyclopentenyl)pentane.

Experimental Part

Synthesis of 1,4-dicyclopentylbutane. Δ^2-Cyclopentenyl chloride was obtained by addition of hydrogen chloride to cyclopentadiene (^{6}); it had b.p. 39–40°/45 mm and 36°/39 mm.

1,4-Dibromobutane was obtained (7) by the action of hydrogen bromide on 1,4-butanediol.

From 216 g (1 mole) of 1,4-dibromobutane and 49 g (2 g-atoms) of magnesium in the presence of 800 ml of abs. ether, a Grignard reagent was obtained. To the resulting complex, under cooling with ice and salt at −5—0°, there were added 193 g (1.9 mole) of Δ^2-cyclopentenyl chloride in 200 ml of abs. ether and 5 g of Cu_2Cl_2. The mixture was stirred for 2 hours at room temperature and for 3 hours while heating on a water bath. After the usual treatment with water and dilute (5—10%) sulfuric acid, the ether layer was washed with water, soda solution, again with water, and dried with calcium chloride. After distilling off the ether, the residue was distilled in vacuo, giving two fractions: b.p. 35—85°/7 mm (A) and b.p. 107—110°/7 mm (B).

From fraction A (35 g), after fractionation on a column* there were isolated 23 g of 1-(Δ^2-cyclopentenyl)but-3-ene (yield 19% of theory) with the following constants: b.p. 150.0°/749 mm; n_D^{20} 1.4492, d_4^{20} 0.8120; found MR_D 40.31; calculated for C_9H_{14} 2F MR_D 40.62.

To confirm the carbon skeleton of 1-(Δ^2-cyclopentenyl)but-3-ene, 10 g of the latter was hydrogenated in the cold in a solution of 15 ml of alcohol in the presence of skeletal nickel** at 75—80 atm of hydrogen. The ob- washed with alcohol and dried over calcium chloride, the hydrocarbon was purified by chromatographic adsorption on 6 g of silica gel. After distillation on a column, *n*-butylcyclopentane was obtained with the following constants: b.p. 155.5°/750 mm; n_D^{20} 1.4320; d_4^{20} 0.7836; literature data (3): b.p. 155.56°/760 mm; n_D^{20} 1.4316; d_4^{20} 0.7846.

Fraction B, isolated from the products of the reaction of Δ^2-cyclopentenyl chloride with tetramethylenedimagnesium bromide in an amount of 99 g, was distilled on a column, and 88 g of 1,4-di-(Δ^2-cyclopentenyl)-butane was isolated (yield 51% of theory)* with the following properties: b.p. 120.5°/7.5-8 mm; n_D^{20} 1.4838; d_4^{20} 0.8849; found MR_D 61.46; calculated for $C_{14}H_{22}$, $2F$, MR_D 61.52.

88 g of 1,4-di-(Δ^2-cyclopentenyl)-butane was hydrogenated in the cold in a solution of 60 ml of acetone in the presence of 15 g of skeletal nickel at a pressure of 75-80 atm. The acetone was washed out with water; the hydrocarbon was dried with calcium chloride, subjected to chromatographic adsorption on 100 g of silica gel, and distilled on a column. After repeated chromatographic adsorption, the resulting 1,4-dicyclopentylbutane had the following constants: b.p. 108°/2.5-3 mm; n_D^{20} 1.46727; d_4^{20} 0.8606; found MR_D 62.56; calculated for $C_{14}H_{26}$, MR_D 62.48.

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* Both here and in the following cases, columns of efficiency 40—45 theoretical plates with a copper packing were used.

** Skeletal nickel prepared by leaching 50% Al from its alloy with Ni (1:1).

Found, %: C 86.75; 86.85; H 13.34; 13.45
$C_{14}H_{26}$. Calculated, %: C 86.60; H 13.40

Synthesis of 1,5-dicyclopentylpentane. 1,5-Dibromopentane was obtained from 240 g of benzoylpiperidine (8), which, in turn, was synthesized by benzoylation of piperidine (9). Since in this synthesis, together with 1,5-dibromopentane, benzonitrile is formed, the presence of which even in an amount of about 1% prevents the reaction of 1,5-dibromopentane with magnesium (2), the latter was subjected to vacuum distillation using a column with a glass packing of efficiency 15 theoretical plates. From 140 g of crude 1,5-dibromopentane, 102 g of product was obtained with the following properties: b.p. 112°/25 mm; n_D^{20} 1.5139; d_4^{20} 1.6985; literature data (10): b.p. 95.5°/10 mm; n_D^{20} 1.5136; d_3^{20} 1.6995.

The reaction for obtaining 1,5-di-(Δ^2-cyclopentenyl)-pentane was carried out as described for the synthesis of 1,4-di-(Δ^2-cyclopentenyl)-butane, from 102 g (0.45 mole) of 1,5-dibromopentane, 24.5 g (1 g-atom) of magnesium, and 91 g (0.9 mole) of Δ^2-cyclopentenyl chloride, without the addition of Cu_2Cl_2. After removal of the ether, the reaction product was separated into two fractions: with b.p. 84-142°/25 mm (A) and with b.p. 142-164°/20-25 mm (B).

Fraction A (22 g) was distilled on a column, whereby 11 g of 1-(Δ^2-cyclopentenyl)-pentene-4 was obtained (yield 16% of theory), with the following constants: b.p. 173.0°/745 mm; n_D^{20} 1.4561; d_4^{20} 0.8186; found MR_D 45.16; calculated for $C_{10}H_{16}$, $2F$, MR_D 45.24.

To confirm that 1-(Δ^2-cyclopentenyl)-pentene-4 indeed contains two double bonds, 1.104 g of the hydrocarbon was hydrogenated in the cold in the presence of 0.1 g of platinum black. In this process 399 ml of hydrogen was absorbed at 744 mm and 19°, or 362 ml under normal conditions. The theoretically required amount of hydrogen for saturation of two double bonds is 364 ml.

To confirm the carbon skeleton of this hydrocarbon, another portion of 1-(Δ^2-cyclopentenyl)-pentene-4 (6 g) was hydrogenated in the cold in a solution of 25 ml of alcohol in the presence of 5 g of skeletal nickel at a pressure of 75-80 atm. The isolated hydrocarbon was subjected to chromatographic adsorption on 5 g of silica gel, after which 5 g of it was distilled on a column. In this way 3 g of *n*-amylcyclopentane was isolated, with the following properties: b.p. 179.0°/749 mm; n_D^{20} 1.4360; d_4^{20} 0.7921. Literature data (3): b.p. 180°/760 mm; n_D^{20} 1.4358; d_4^{20} 0.7912.

Fraction B, in an amount of 45 g, was also fractionated on a column. This gave 27 g of 1,5-di-(Δ^2-cyclopentenyl)-pentane (30% of theory), with the following properties: b.p. 151.5°/12 mm; n_D^{20} 1.4849; d_4^{20} 0.8920; found MR_D 65.63; calculated for $C_{15}H_{24}$ 2F, MR_D 65.93.

* Without the use of Cu_2Cl_2, the yield of 1,4-di-(Δ^2-cyclopentenyl)-butane was 47%.

27 g of 1,5-di-(Δ^2-cyclopentenyl)-pentane was hydrogenated in the cold in the presence of 15 g of skeletal nickel in a solution of 50 ml of acetone at a pressure of 75–80 atm. The resulting 1,5-dicyclopentylpentane was purified analogously to 1,4-dicyclopentylbutane, giving a product with the following constants: b.p. 154.0–154.5°/12–12.5 mm; n_D^{20} 1.46816; d_4^{20} 0.8604; found MR_D 67.18; calculated for $C_{15}H_{28}$, MR_D 67.07.

Analysis:

Found, %:	C 86.35; 86.21;	H 13.51; 13.52
$C_{15}H_{28}$. Calculated, %:	C 86.54;	H 13.46

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Note: Figure translations are in progress. See original paper for figures.