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Abstract

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A. F. PLATÉ and V. I. STANKO

ON THE INTERACTION OF THE IOTSICH REAGENT WITH Δ^2-CYCLOPENTENYL CHLORIDE

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In view of the fact that cyclopentane hydrocarbons of the general formula

$$\text{cyclopentenyl} - (\text{CH}_2)_n - \text{cyclopentenyl}$$

have been insufficiently studied, we undertook the synthesis of some of these hydrocarbons. In particular, to obtain 1,2-dicyclopentylethane, one member of this series, it was planned to use the reaction between Δ^2-cyclopentenyl chloride and the Iotsich reagent. The latter, as is known, consists predominantly of acetylenedimagnesium bromide (according to Grignard and co-workers (^{1}), up to 95%) and a certain amount of acetylenemonomagnesium bromide.

Table 1

Interaction of Δ^2-cyclopentenyl chloride with the Iotsich reagent

Experiment No.	Ethyl bromide, mol.	Magnesium, mol.	Cyclopentenyl chloride, mol.	Yield (I), g	Yield (I), % of theory	Yield (II), g	Yield (II), % of theory
1	1	1	0.8	19	31	not isolated	not isolated
2	2	2	1.25	35	36	20	35
3	2	2	2	32	20	28	29
4	2	2	1.6*	37	30.5	21	28

* 4 g of cuprous chloride was added to the reaction mixture.

From the literature data it is known that the Iotsich reagent reacts only with difficulty with haloalkyls. For example, under the action of ethyl bromide on acetylenedimagnesium bromide, hexine-3 is formed in only 20% yield (^{2}). Usually the interaction of the Iotsich reagent with haloalkyls is accompanied by side reactions, the principal ones being the elimination of hydrohalic acid from the haloalkyl and the reduction of the haloalkyl to the corresponding alkane. Thus, in the interaction of acetylenedimagnesium bromide with *n*-butyl bromide, a considerable amount of butylene and butane is formed, while in the interaction with *n*-octyl bromide the main product of the reaction is *n*-octane (^{3}). There is no information in the literature on the interaction of the Iotsich reagent with halo derivatives of cyclic hydrocarbons.

In Δ^2-cyclopentenyl chloride, which is readily obtained from cyclopentadiene, the chlorine atom is in the allylic position and is therefore highly reactive. For this reason, Δ^2-cyclopentenyl chloride has repeatedly been used in reactions with magnesium haloalkyls for the purpose of obtaining Δ^2-alkylcyclopentenes (^{4}). In the present work we have studied the interaction of Δ^2-cyclopentenyl chloride with the Iotsich reagent and have shown that this gives di-Δ^2-cyclopentenylacetylene (I) in an amount of

20–36%; however, approximately the same amount (28-35%) of Δ^2-cyclopentenylacetylene (II) is formed simultaneously.

$$\Delta^2\text{-cyclopentenyl}{-}C{\equiv}C{-}\Delta^2\text{-cyclopentenyl} \tag{I}$$

$$\Delta^2\text{-cyclopentenyl}{-}C{\equiv}CH \tag{II}$$

Attempts to change the reaction conditions (different relative amounts of the reagents, introduction of cuprous chloride as a catalyst) did not lead to an increase in the yield of di-Δ^2-cyclopentenylacetylene. The data obtained are summarized in Table 1.

The constant amount of both possible reaction products, irrespective of the amounts of reagents taken, and the considerable yield of Δ^2-cyclopentenylacetylene should apparently be explained by the different rates of interaction of Δ^2-cyclopentenyl chloride with both possible organomagnesium compounds:

$$\mathrm{BrMgC{\equiv}CMgBr};$$

$$\mathrm{BrMgC{\equiv}C}{-}\,{}^{2}\text{-cyclopentenyl}$$

As Δ^2-cyclopentenyl chloride is added to Iotsich’ s reagent, magnesium salts precipitate, the reaction mass thickens, and the reaction stops, although both organomagnesium compounds as well as the chloride are still present in the mixture. The excess of the latter gradually turns into a polymeric resin with evolution of hydrogen chloride.

In one experiment, after approximately half of the required amount of Δ^2-cyclopentenyl chloride had been added to Iotsich' s reagent, cyclopentanone was added, which, as is known (^{5}), can give up to 77% of the corresponding glycol with this reagent. After decomposition of the reaction mixture, all possible reaction products were found in it, namely: Δ^2-cyclopentenylacetylene, di-Δ^2-cyclopentenylacetylene, and also the tertiary alcohol

$$\Delta^2\text{-cyclopentenyl}-C\equiv C-C(OH)(\text{cyclopentyl}) \qquad \text{(III)}$$

and the glycol—1,2-di-(1-hydroxycyclopentyl)acetylene.

$$\text{HO}-\text{C}(\text{cyclopentyl})-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{cyclopentyl}) \qquad \text{(IV)}$$

The presence of the latter two compounds proves that, at the moment when cyclopentanone was added, both the mono- and the dimagnesium compounds were present in the reaction mixture.

The di-Δ^2-cyclopentenylacetylene (I) obtained by us is an isomer of the previously synthesized hydrocarbon with a conjugated system of multiple bonds, di-Δ^1-cyclopentenylacetylene,

$$\Delta^1\text{-cyclopentenyl}-C\equiv C-\Delta^1\text{-cyclopentenyl}$$

which has m.p. 58.5-60° and b.p. 105-110° at 2 mm (^{5}).

Hydrogenation of the di-Δ^2-cyclopentenylacetylene obtained over charcoal under hydrogen pressure in the presence of Raney nickel gave the saturated hydrocarbon 1,2-dicyclopentylethane.

Experimental Part

Iotsich' s reagent was prepared by the method described by Pinkney and Marvel (^{5}). Cyclopentenyl chloride was obtained by addition of hydrogen chloride to cyclopentadiene (^{6}).

Reaction of the Iotsich reagent with cyclopentenyl chloride. The results of the experiments carried out are given in Table 1. A description of experiment 4 is given below. In a two-liter flask equipped with a stirrer, dropping funnel, and reflux condenser, the magnesium derivative was prepared from 2 mol of ethyl bromide and 2 g-at. of magnesium in 1.2 l of abs. ether. Acetylene (about 30 l) was passed through the solution of the organomagnesium complex until clear separation of the Iotsich reagent and ether occurred. With the flask containing the reaction mixture cooled with ice and salt to −10°, −15°, 164 g (1.6 mol) of Δ^2-cyclopentenyl chloride in 200 ml of abs. ether was added dropwise, and then 4 g of cuprous chloride, after which the mixture was stirred for another 3 hours at room temperature and for 6 hours with heating on a water bath. To decompose the complex, with cooling by ice and salt, 200 ml of water was added, and then 300 ml of dilute sulfuric acid. The ether layer was washed with water, sodium carbonate solution, again with water, and dried with calcium chloride. After removal of the ether, the forerun was distilled off in a slight vacuum up to 90° at 90–100 mm. As a result of fractionation of this cut with a 40 theoretical-plate column, 21 g (28% of theory) of Δ^2-cyclopentenylacetylene (II) was isolated, with the following properties: b.p. 97.2° at 752 mm; $n_D^{20} = 1.4363$, $d_4^{20} = 0.8014$; found $MR_D = 30.10$; for C_7H_8F, |= calculated MR_D 29.80.

To prove the structure of Δ^2-cyclopentenylacetylene, 15 ml of the hydrocarbon was hydrogenated in alcoholic solution (25 ml) in the cold in the presence of 5 g of skeletal nickel under hydrogen pressure. Ethylcyclopentane was obtained with the following properties: b.p. 102.8° at 750 mm; $n_D^{20} = 1.4198$; $d_4^{20} = 0.7668$. Literature data (7): b.p. 103.466° at 760 mm; $n_D^{20} = 1.41981$; $d_4^{20} = 0.76647$.

After removal of Δ^2-cyclopentenylacetylene from the reaction mixture, in a deeper vacuum a fraction with b.p. 96–102° at 8 mm was distilled in an amount of 37 g; it was redistilled in vacuum with a 15 theoretical-plate column. Thirty-two grams of di-Δ^2-cyclopentenylacetylene (I) was obtained, with the following properties: b.p. 106°/9–9.5 mm; $n_D^{20} = 1.5172$; $d_4^{20} = 0.9596$; found $MR_D = 49.83$; for $C_{12}H_{14}F$, |= calculated MR_D 50.20.

To prove its structure, 15 ml of di-Δ^2-cyclopentenylacetylene was hydrogenated in the cold in an autoclave at 70–80 atm in a solution of 75 ml of ethyl alcohol in the presence of 15 g of Raney nickel. The resulting catalyzate was washed with water to remove the alcohol, and, to free it from traces of unsaturated hydrocarbons, was subjected to chromatographic adsorption on 15 g of silica gel. Fourteen milliliters of product was obtained, which was distilled in vacuum with a 40 theoretical-plate column. After fractionation, 12 ml of the hydrocarbon was again subjected to chromatographic adsorption on 10 g of silica gel. Ten milliliters of 1,2-dicyclopentylethane was obtained, with the following properties: b.p. 92° at 8–8.5 mm; $n_D^{20} = 1.46628$; $d_4^{20} = 0.8620$; found MR_D 53.33; for $C_{12}H_{22}$ calc. MR_D 53.23. The literature gives the following data for this hydrocarbon, obtained by another method (5): b.p. 109–110° at 17 mm; $n_D^{20} = 1.4657$; $d_4^{20} = 0.8633$.

Reaction of the Iotsich reagent with Δ^2-cyclopentenyl chloride and cyclopentanone in two stages. To the Iotsich reagent, prepared as described above from 2 mol of ethyl bromide and 2 g-at. of magnesium in 1.2 l of abs. ether, with cooling by ice and salt, 76 g (0.75 mol) of Δ^2-cyclopentenyl chloride in 150 ml of abs. ether was added dropwise. The mixture was stirred at room temperature for 4 hours, after which, with cooling, 63 g (0.75 mol) of cyclopentanone in 150 ml of abs. ether was added. The reaction mixture was stirred for 3 hours at room temperature and for 4 hours with heating on a water bath. Decomposition and further work-up were carried out as in the preceding experiment.

There were isolated 7 ml (~6 g) of Δ^2-cyclopentenylacetylene (II) (b.p. 97–98°;

$n_D^{20} = 1.4365$) and a broad fraction with b.p. 122–170° at 14 mm (57 g), which crystallized in the receiver. This fraction was dissolved in 100 ml of alcohol and hydrogenated cold under a hydrogen pressure of 70–80 atm in the presence of 15 g of skeletal nickel. After distilling off the alcohol, the residue was distilled in vacuum:

fraction 1	b.p.	92–125° at 5 mm	— 22 g
fraction 2	» »	125–150° » 5 »	— 23 »
fraction 3	» »	150–154° » 4.5–5 »	— 8 »

From fraction 1, after redistillation, 11 ml (~9 g) of 1,2-dicyclopentylethane was obtained (b.p. 87° at 6 mm; $n_D^{20} = 1.4668$; $d_4^{20} = 0.8640$), and the residue was added to fraction 2. Assuming that it might contain the tertiary alcohol (V), we subjected it to dehydration with oxalic acid, and then to cold hydrogenation with Raney nickel under pressure, considering that the reaction would proceed according to the scheme:

$$\underset{(V)}{\text{cyclopentenyl-CH}_2\text{-CH}_2\text{-C(OH)(cyclopentenyl)}} \xrightarrow{-\mathrm{H_2O}} \underset{(VI)}{\text{cyclopentenyl-CH}_2\text{-CH}_2\text{-cyclopentenylidene}} \longrightarrow$$

$$\xrightarrow{+\mathrm{H_2}} \text{cyclopentyl-CH}_2\text{-CH}_2\text{-cyclopentyl}$$

Indeed, after purification of the catalyst by chromatographic adsorption on silica gel and distillation, 8 g of 1,2-dicyclopentylethane were obtained (b.p. 92° at 8 mm; $n_D^{20} = 1.4664$; $d_4^{20} = 0.8625$).

Fraction 3 was recrystallized twice from acetone. There were obtained 6 g of the glycol 1,2-di(1-hydroxycyclopentyl)ethane with m.p. 131–132°. Literature data for this glycol[8]: m.p. 131.2–132.4°.

Found, %:	C 72.67;	H 11.19
$C_{12}H_{22}O_2$. Calculated, %:	C 72.71;	H 11.12

This glycol apparently formed as a result of hydrogenation of glycol IV.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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