The Reactions with Cyclic Ketones

E.M. Gadirova, H.F. Hajiyeva, U.N. Rustamova, H.L. Rafieva, A.A. Samadova
Baku State University

Abstract: In the viewed article, the factors that influence on the reaction of ferrocene with some cyclic ketones and the yield of product were researched and it was found out that, the process goes at acidic medium. The elemental analysis of obtained compounds was carried out, the structures were researched by IR and PMR-spectra.

Keywords: ferrocene, ketones, cyclopentanone, cyclohexanon and others.

Ferrum dicyclopentadienes and their derivatives posses many important properties. That is why these compounds are being used in pharmacy, petroleum chemistry, in preparation of anti-corrosion materials and et cetera. Compounds derived from ferrocene – alkyl, aryl derivatives, carbonyls, ethers and esters are of special interest [1].

Reactions between aliphatic ketones and ferrocene in the presence of catalyst H_{2}SO_{4}/DEAN (2:1) have been conducted and corresponding ferrocenylicarbonyls have been synthesized [2].

Tab1. Results reactions ferrocene with cyclic ketones

<table>
<thead>
<tr>
<th>Phase</th>
<th>The phase-forming components</th>
<th>Ratio of components</th>
<th>Reactive components</th>
<th>The addition products</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic</td>
<td>petroleum ether</td>
<td>10</td>
<td>ferrocene and cyclopentanone</td>
<td>ferrocenylcyclopentyl (cyclohexylcarbinols)</td>
</tr>
<tr>
<td>inorganic</td>
<td>water</td>
<td>1</td>
<td>catalyst H_{2}SO_{4} and its transporter</td>
<td>catalyst H_{2}SO_{4} and its transporter</td>
</tr>
</tbody>
</table>

As a follow-up to research reaction between cyclic ketones and ferrocene has been analyzed. The yield was 18-20% .

\[ \text{Fe} + \text{H}_{2}\text{SO}_{4}/\text{DEAN} \rightarrow \text{Fe} + \text{OH} \]
\[ \text{t} \ 58-60^\circ \text{C} \]

\[ \text{Fe} + \text{cyclic ketone} \rightarrow \text{Fe} + \text{OH} \]
\[ \text{t} \ 68-71^\circ \text{C} \]
The Reactions with Cyclic Ketones

It is known that reaction of aliphatic ketones with ferrocene is easier than that of cyclic ketones, and yield is higher. It is worth noting that there are many questions concerning production of ferrocenylcyclokarbonyls. For this purposes, it has been tested to use derivatives of ferrocene by substituting metals, for example, C₃H₃FeC₃H₃Li or C₃H₃FeC₃H₃MgHal and corresponding cyclic ketones in the THF solvent. The yield was 26-28% [3].

When comparing the reactions that are shown above, it has been observed that ferrocenyl cyclopentanol (1) has better yield than ferrocenyl cyclohexanol (2). All of cyclic ketones bearing 4 carbon atoms (cyclobutanols) does not take part in these reactions. There is strain since the angle between C-atoms is much smaller than normal tetrahedr, which is 109°28’. Due to the Bayer strain in 5- and 6- memered cycles (0°, 44') system is somewhat unstable. The strain in 6-membered cycles is about (-5°, 16°).

Best result has been obtained on cyclohexanone. Due to the existence of α,β-conformations cyclohexanone is stable, so that, there has been monosubstitution in nucleus of ferrocene and ferrocenyl cyclohexanol (2) has been produced. Main conditions required for reaction are: acidic medium, and maintainence of temperature at required level. Since the reaction is exothermic, the temperature of medium increases by time and Van-der-Waals forces between ketones are being weakened. Due to deformation of molecule structure the yield of reaction decreases. On the other hand, we must also take into account steric factors, because they are the reason for low yield of aliphatic ketones in comparison with cyclic. We would like to note that we have also carried out the similar reactions with aliphatic ketones and the yield was about 75-78%. The conditions, nature of catalyst, its concentration, temperature of system and other factors must be taken into account too[4].

The reaction of hydrogen sulfide and some mercaptanes with both aliphatic and aromatic ketones has been analyzed. In such case, foul-smelling ferrocenylthioethers has been obtained. These compounds are solved in nearly all of organic solvents, especially benzene. This property can be utilised in order to clean some oils containing mercaptane or its fractions [5].

Because of the fact that, in the reaction, the yield of (1) and (2) are lower means that there is considerable amount of loss, and as we noted before, it can be explained by the deformation of molecules taking part in reaction, which leads to less productive collisions.

In the case described above, the reactive abilityis lower according to cyclopentanone, so the reaction product of (1) is less than (2). 92-94% H₂SO₄ has been used as catalyst purposes. The main purpose of using concentrated acid is because of creating acidic medium and speeding up the process due to the oxidative property. As we mentioned, reaction happens in acidic medium. Obtained ferrocenyl cyclopentanol (1) and ferrocenyl cyclohexanol (2) has been washed by distilled water few times and dried under the air for a day. Both products are orange powder with specific smell.

Brutto formula of compound (1) is C₁₃H₁₇FeO and that of (2) is C₁₆H₂₀FeO. Elemental analysis of compounds (1) and (2) gives the following results:

<table>
<thead>
<tr>
<th>Compound</th>
<th>C%</th>
<th>H%</th>
<th>O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₃H₁₇FeO</td>
<td>66.66</td>
<td>6.61</td>
<td>5.92</td>
</tr>
<tr>
<td>C₁₆H₂₀FeO</td>
<td>67.60</td>
<td>7.04</td>
<td>5.63</td>
</tr>
</tbody>
</table>

The IR spectral analysis of ferrocenylocyclopentanol (1) and ferrocenylcyclohexanol (2) has been run. The peaks for OH residue was observed on vOH 3420-3480 cm⁻¹ for (1) and vOH 3450-3510 cm⁻¹ on (2). The peaks for ketone (CO) residue has not been observed on the characteristic vOH (1680-1690 sm⁻¹) area. It shows that original ketone used as reagent has been consumed to get alcohol, whereas rest has undergone some transformations. When same reactions were carried out for aliphatic ketones the signals for ketone (CO) residue was still absent. Moreover it has been observed that OH residue on ferrocenylcarbonyl is of dual nature.

On the NMR spectrum of unsubstituted ferrocene, because of symmetric nature of cyclopentadiene (C₅H₅) ligands the protons had signals at 4.30 ppm. After the substitution the protons of unsubstituted cyclopentadiene was at 4.17 ppm, while that of substituted cyclopentadiene was at 4.57 ppm and 4.55 ppm for the α and β protons respectively.

The NMR spectra was taken in CCl₄ solution and TMS was used as standard reference [5].
As a conclusion of study of NMR and IR spectra of ferrocenylnocarbonyls, it has been learned that there are two OH groups in these metalcomplexes. One of them is in intramolecular coordination with central Fe atom, while another OH is free.

REFERENCES