Chapter 09

Advanced Materials, Artificial Intelligence, and Sustainable Technologies for Energy and Environmental Engineering
ISBN: 978-9915-704-10-4
DOI: 10.62486/978-9915-704-10-4.ch09
Pages: 119-130

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Ecological Basis for the Use of Iron and Manganese-Based Metal Complexes

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ABSTRACT

A series of reactions were carried out in the interfacial H_2SO_4/DEAN catalytic environment based on ferrocene and cymantrene, and new derivatives were synthesized. The obtained derivatives exhibited antidetonation properties. DEAN-diethylammoniumnaphthenate-$(C_2H_5)_2NHCOOR$ (R-naphthene residue), which plays the role of a carrier in the process, is obtained from the interaction of diethylamine $(C_2H_5)_2NH$ with naphthenic acid. The main feature of this compound is that it reacts with strong acids, in our case concentrated sulfuric acid, to form an intermediate complex, and then enters into ion exchange reactions. Using this property of them, it was possible to use them in interphase catalysis reactions. In this regard, by using DEAN, it was possible to overcome the immiscible interphase barriers by transferring one of the reactants from the aqueous medium to the organic phase. In this case, by using a carrier, it was possible to ensure the solubility of organometallic compounds in organic solvents, taking into account the hydrophobicity of the compounds, and to increase the yield of the reaction product. As a result, the yield of the reaction product was relatively high.

Keywords: Cyclic Ketone; DEAN; Sulfuric Acid; Interfacial Catalysis; Ferrocene; Cymantrene.

INTRODUCTION

The use of additives in fuels is very important. What is more important is how the additives added to fuels affect the environment from an ecological perspective. Until 1980, tetraethyllead (TEL), which was widely used as an additive in fuels, polluting the environment and causing very serious diseases in the human body, completely limited the possibilities of using this substance. Tetraethyllead was very profitable as an additive, it was added in an amount of 0,5-0,8 g per 1 kg of gasoline. Since it has an ecologically toxic and carcinogenic effect, many countries banned its use in accordance with Euro-2 standards at that time, and only then did research begin on many substances for use as anti-knock additives.

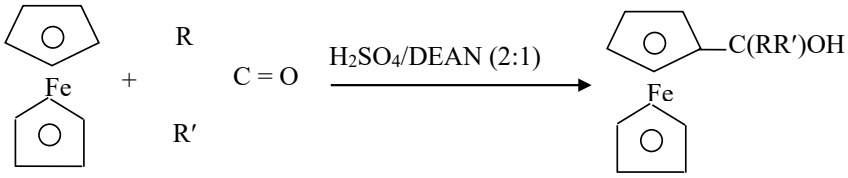
In our modern era, the requirements of Euro-5 standards are completely different. Better yet, the use of electric vehicles with zero pollution for the environment is one of the main requirements of the modern era. However, since a complete transition to electric vehicles is economically difficult, new standards must be developed to make fuel-powered engines safe or at least slightly dangerous for the environment. In this case, the main issue facing us is the development of environmentally friendly additives that are as harmless as possible to the environment. In this direction, the use of organometallic compounds and derivatives based on them has been one of the main directions in finding a solution to environmental problems. As the metal contained in organometallic compounds converts the oxygen that provides combustion into more effective atomic oxygen, it is also added to the fuel in a very small amount (37 mg/

ml). This makes the use of these substances efficient and prevents the formation of metal oxides, even in small quantities, during combustion in the process. It should be noted that the industrially produced cement-based anti-knock additive composition produced by the German company "hi-tech", as well as the FK-4 ferrocene-based compositions of the Russian "Khimki" plant, have wide production and application areas in many oil refining production areas.

The possibility of using more effective additives for environmental protection is always on the agenda. As the demand for gasoline and diesel fuel has increased in recent years, it is very important to have environmentally friendly additives. For this purpose, we have investigated the possibilities of using organometallic compounds in motor transport. The most widely used representatives of organometallic compounds: ferrocene and cymantrene have been the main objects of our research.

Many substances based on ferrocene and cymantrene have anti-knock properties. On the other hand, these compounds, like octane number enhancers, also have a smoke-reducing effect by ensuring normal engine operation. In order to increase the compression resistance of low-octane motor fuels, a large amount of additives is required. In this case, certain problems arise: as a result of the deposition of metal oxides in the combustion chamber and on the surface of the burning spark plugs, the engine fails and eventually becomes unusable from an ecological point of view. In order to ensure normal engine operation, the amount of metal in various brands of gasoline is determined according to international standards. According to these standards, the amount of iron is 17-37 mg/l, and the amount of manganese is 28-55 mg/l. This amount is also considered useful from an ecological point of view. In order to reduce the amount of metals (Fe, Mn) in ferrocene and simantrene molecules, alkyl and oxyalkyl groups that do not have an antiknock effect are introduced into the molecules. For this purpose, alkylation reactions of ferrocene and simantrene were carried out based on Friedel-Crafts reactions. For the first time, we used pyrocondensate, which is a pyrolysis product of naphtha gasoline, for the alkylation of ferrocene. Pyrocondensate contains 32-35 % unsaturated hydrocarbons of various structures.

Below is the synthesis reaction of ferrocene-based derivatives in an interfacial catalytic environment. Here, depending on whether the ketone used is aliphatic or cyclic, the yield of the reaction product varies. Thus, when H_2SO_4/DEAN was used in a 2:1 ratio, the corresponding ferrocenylcarbinols were obtained in high yields with aliphatic and cyclic ketones.[1,2]



70–85% (1)

R=R′=CH_3

It should be noted that the reactions considered were first carried out in the presence of concentrated H_2SO_4 acid. The course of the process is described below.

METHOD

A three-necked flask with a volume of 0,5 liters is blown with nitrogen. After adding 15 ml of pungent-smelling cyclohexanone (cyclopentanone) to the flask, it is cooled to -10^0 C under cold

conditions with an ice-cold NaCl (salt) solution, and 20 ml of 92 % H_2SO_4 acid, previously cooled to -10^{0}C, is added to it. Then the mixture is stirred in a mixer for 30 minutes. It should be noted that the process is exothermic, so it proceeds with the release of heat. This has a negative effect on the course of the reaction and the yield of the reaction product.

Therefore, the process is carried out with constant cooling with ice water (-10^{0}C). The color of the mixture is light yellow, but gradually the color becomes brown and dark. Then, with stirring in a medium-speed mixer every 10 minutes, ferrocene in the form of an orange powder with a total mass of 9,8 grams is added in portions to the reaction mixture. Stirring is carried out until the dark brown color obtained in the process (a greenish color is visible on the walls of the beaker) remains unchanged, stirring continues for about two and a half hours. The reaction mixture obtained in this way is neutralized in parts with a solution of $NaHCO_3$ (baking soda). At this time, foam forms on the solution. Through the baking soda, the carbinol derivative of ferrocene rises to the solution through the foam. The foam is collected by filtration, washed several times with distilled water, and dried in a drying cabinet. In the process, a solid substance, ferrocenylcyclocarbinol, is obtained, which changes color from orange to yellowish. The obtained substance has a specific odor. The soda solution used as a neutralizer is prepared as follows:

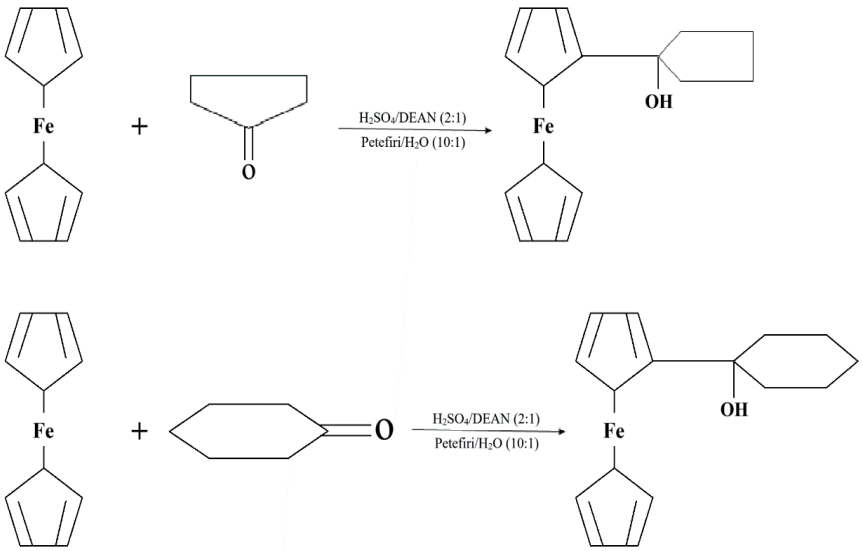
$NaHCO_3$ (baking soda) was added in portions to one liter of distilled water previously placed in the refrigerator and mixed. Then, this solution was added in portions (10 ml) to the reaction mixture. At this time, the foam that formed on the surface of the solution brought the newly formed yellow substance to the solution. It was collected through a skimmer into a filter covered with a sieve, washed once or twice with cold distilled water, and dried in a drying cabinet. A total of 22-23 grams of $NaHCO_3$ baking soda were used in the process. After drying, the powder was weighed on an analytical balance and the amount of reaction product was calculated based on the molar amount of ferrocene. Since the yield was not high, the same reaction was also carried out in an interfacial catalysis environment.

Thus, concentrated sulfuric acid and diethylammonium naphthenate were used to create the interphase medium. These substances were taken in different ratios and the best result was obtained in the ratio H_2SO_4/DEAN 2:1. The process flow is given below.

The same reaction was carried out in the presence of diethylammonium naphthenate (DEAN), a viscous and dark brown substance. The synthesis process was carried out as above, but the difference was that two phases were used in the course of the reaction. For this, 30 ml of petroleum ether with a specific odor, boiling at 30^0–70^{0}C, was taken. 15 ml of cyclic ketone (cyclopentanone or cyclohexanone), 9,8 g of orange-colored powder-ferrocene were added to it and mixed. At this time, no reaction occurred. 20 ml of 92 % H2SO4 solution was added to this mixture, then 10 ml of brown viscous diethylammonium naphthenate (DEAN). In the process, 92 % sulfuric acid served two functions: sulfuric acid was used both as a catalyst and to neutralize the acidic environment. The inorganic phase was transparent, and the organic phase was colored chestnut after the addition of ferrocene. At the boundary (separating boundary) of these two phases, brown DEAN was located. After heating the flask to 10^{0}C, the onset of the reaction was observed. Since, as we mentioned above, the process is exothermic, it was sufficient to initially heat the flask to a temperature of 10^{0}C for the reaction to proceed. The onset of the reaction was determined by the gradual browning of the transparent color in the inorganic phase. First, 92 % sulfuric acid was added to the inorganic phase, that is, water, and then petroleum ether. At this time, the organic and inorganic phases separated. When left

to stand, the organic phase formed in the upper part of the flask, and the inorganic phase in the lower part. After the phase separation was complete, a cyclic ketone (cyclopentanone or cyclohexanone) was added to the organic phase, i.e. the upper phase, and then a metal organic compound (ferrocene or cymanthrene) in a 1:1 molar ratio. Only then was the carrier DEAN-diethylammonium naphthenate $(C_2H_5)_2NHOCONaf$ added to the system to initiate the reaction. The process was carried out by heating at positive temperatures: in the temperature range of 20-40^{0}C. Thus, the preparation of the corresponding derivatives of organometallic compounds with cyclic ketones using a phase-shifting catalytic medium ensured, on the one hand, its one-step process, and, on the other hand, its loss-free and high-yield preparation. At the same time, the purity of the obtained substance was also high. The yield of the reaction product obtained by this method was up to 85 %.

The main purpose of DEAN in the process was to transport H2SO4 acid to the organic phase. It should be noted that, although H2SO4/DEAN was taken in different ratios, the most optimal state was observed at a ratio of 2:1. When the ratio was 2:1, DEAN was able to transport H_2SO_4 acid to the organic phase in catalytic amounts. After the solid H_2SO_4 acid, which was involved as a catalyst in the process, passed into the organic phase, the interaction of ferrocene with cyclic ketones (cyclopentanone and cyclohexanone) occurred in the organic phase. In this regard, sulfuric acid was used as a catalyst in the process and to create an acidic environment. In order to separate ferrocenylcyclocarbinol from the upper part of the flask, i.e. from the organic phase, 4-5 ml of a 1 liter pre-prepared cold 5 % $NaHCO_3$ solution was added to that phase in portions and mixed. Due to the CO_2 gas released from the reaction mixture during each mixing, the reaction product appeared on the surface of the solution in the form of a yellow foam. The yellow foam was collected on a sieve with a perforated skimmer and washed 1-2 times with cold distilled water. The observed reaction was completed in exactly 1 hour and 30 minutes. The obtained substance was dried in a drying cabinet for 24 hours. Then, the purity of the obtained substances was checked using the thin layer chromatography method. Thus, the reactions of ferrocene with cyclic ketones under interfacial catalysis conditions of H_2SO_4/DEAN (2:1 ratio) were carried out and the corresponding derivatives were synthesized.[1] The optimal temperature during the reaction was taken between 20-40^{0}C, at which time the yield of the reaction product was obtained between 70-85 %.[3] The temperature used during the reaction directly affected the yield of the reaction product.



(2)

If the temperature is too low during the reaction, the reaction does not occur, and the flask must be slightly heated to start the process. At high temperatures (above 40^0C), the yield of the reaction product is very small, 20-22 %, due to the decomposition of the metal-organic complex. [4] Compounds obtained based on cyclic ketones have occurred in the same interfacial catalysis environment as aliphatic ketones.[5,6,7]

The general formula for organometallic compound (I) was $C_{15}H_{18}FeO$, and for compound (II) it was $C_{16}H_{20}FeO$. The results of elemental analysis of the organometallic compounds under consideration are given below:

$C_{15}H_{18}FeO$ C% 66,66 H% 6,61 O% 5,92 $C_{16}H_{20}FeO$ C% 67,60 H% 7,04 O% 5,63

Interpretation and discussion of the results

It is known that the reactions of ferrocene and cymanthrene occur more easily with aliphatic ketones than with cyclic ketones, and the yield is higher than with them. This can be explained by the spatial structure of the substance. The yield of the product in the reactions under consideration was therefore low. It was possible to increase the yield of the reaction product by using lithium or magnesium derivatives of ferrocene and cymanthrene.[8] On the other hand, it was found that when both ferrocene and simantrene react with cyclic ketones, the temperature factor greatly affects the process, so it is possible to keep it under constant control and obtain a product with a high yield. For this purpose, reactions were carried out by selecting different conditions. It should be noted that by choosing the right temperature, it was possible to increase the yield of the reaction product up to 85 %. Thus, by choosing the right temperature, it is possible to increase the yield of the reaction product by 3-4 times. The reaction mixtures were taken in certain proportions and placed in certain phases in sequence.

Toluene and a lithium-substituted derivative of ferrocene were used as phase-forming media. It should be noted that the yield of the reaction product was not high in this case, 23-28 %. However, when studying the factors affecting the course of the reaction, it was determined that the most important thing for the process to proceed in one direction is the correct selection of the reaction medium and the temperature factor. Otherwise, the reaction becomes reversible and the yield of the product decreases. On the other hand, the reason for the low yield of the reaction product is that the active Grignard reagent $C_5H_5FeC_5H_4MgX$ dimerizes to form the symmetrical compound $(C_5H_5FeC_5H_4)_2Mg$. At this time, its reactivity decreases.

$$2\ C_5H_5FeC_5H_4MgX \rightarrow (C_5H_5FeC_5H_4)_2Mg + MgX_2 \qquad (3)$$

The removal of derivatives obtained from the reactions of organometallic compounds with cyclopentanone and cyclohexanone from the reaction mixture poses certain difficulties. Thus, choosing the right environment is also very important for the lossless removal of the organometallic compound cyclopentanol and cyclohexanol mixture from the reaction mixture. Thus, after the reaction is complete, the hydrolysis of the product obtained from the reaction mixture was carried out by creating a weakly acidic environment. At this time, the alkaline solution $Mg(OH)_2$ or XMgOH (X-organic radical) formed acted on the ferrocene nucleus and caused the iron in the molecule to oxidize to the Fe^{+2} cation, resulting in the complete decomposition of the ferrocene molecule. This means that the iron and cyclopentadienyl rings are separated from each other. Therefore, the method of decomposition of part of the product as a result of hydrolysis of the reaction product was not considered suitable. Also, the formation of intermediate products in the reaction reduces the yield of the reaction product. Regarding the yield of the reaction

product, when investigating the reason for the low reaction product, it was determined that the metallizing effect of the magnesium compound is low at low concentrations. Also, the reaction product is subject to decomposition when stored for a long time. In this regard, based on these shortcomings, the method was not considered suitable. For this, it was necessary to develop a more suitable method, and for this purpose, an interphase environment was created. In this case, the process was carried out using organic and inorganic phase-forming substances. Thus, an immiscible two-phase system was created and the direct reaction of organometallic compounds with cyclic ketones was carried out. In other words, the synthesis of organometallic compounds with cyclopentanone and cyclohexanone was carried out in an interfacial catalytic environment. When creating an interfacial environment, the resulting two-phase system should not mix with each other. For this purpose, petroleum ether, a light fraction of gasoline, was used as the organic phase, and water was used as the inorganic phase. The ratio of petroleum ether to water was taken as 10:1 by volume (figure 1)

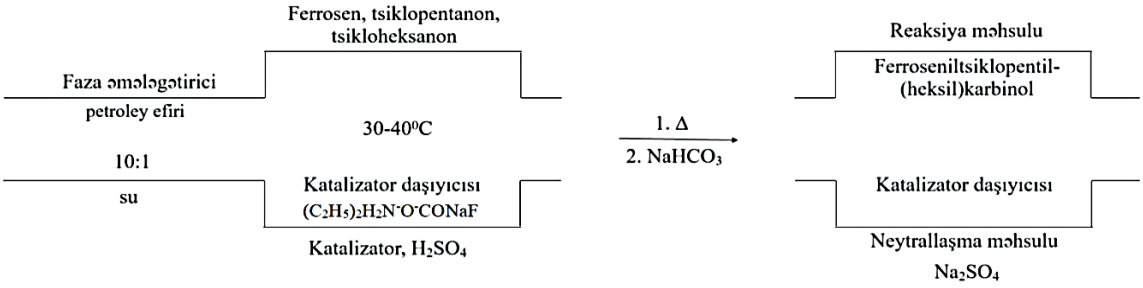
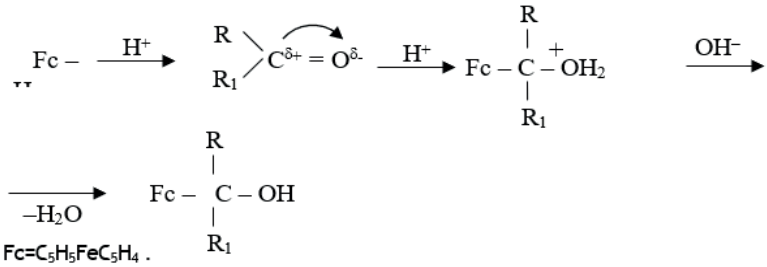


Figure 1. Description of the interfacial catalytic environment

Both ferrocene and cymanthrene react with ketones via an electrophilic substitution mechanism. Since the cymanthrene molecule is easily decomposed, reactions with ferrocene have been studied more extensively. It has been shown that the hydrolysis ability of the intermediate carbocation obtained in the process, as well as the steric factors created by this carbocation, directly affect the yield of the reaction product. These reactions with cymanthrene occurred in a much lower yield than with ferrocene. This was explained by the decomposition of the cymanthrene molecule in the presence of concentrated sulfuric acid during the reaction and the failure of the reaction. Corresponding reactions with simantrene were also carried out in the presence of hydrochloric and phosphoric acids, but no positive results were obtained.

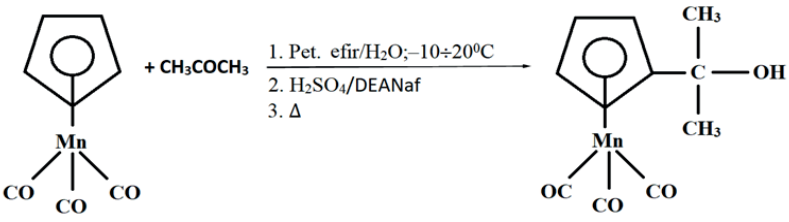
The mechanism of these reactions in an acidic environment can be generally described as follows:[9]



During the reaction, ketones and sulfuric acid were taken in different ratios. The correct selection of these ratios directly affects the yield of the reaction product obtained. In an acidic environment, it was more expedient to take the ratio of ketones to sulfuric acid (92 %) as 45

ml:15 ml. The main purpose of taking sulfuric acid at a high concentration was to prevent the hydrolysis of the intermediate complex obtained from the interaction of the ketone with the acid. At lower concentrations, the intermediate complex obtained usually decomposes. The kinetics of the process was studied based on the formation of the corresponding ferrocenylcarbinol between ferrocene and acetone. In order to study the kinetic regularities of the process, the reaction between the aliphatic ketone acetone and ferrocene was studied in detail. In the presence of diethylammonium naphthenate and sulfuric acid (1:2) in the interfacial catalysis medium, the reaction of acetone to ferrocene proceeded at an increasing rate for two hours, and then a gradual weakening of the rate was observed. The process was carried out for about two hours in total. In the process, 85-87 % of ferrocene entered the combination reaction, and the rest was decomposed for certain reasons. When studying the kinetics of the process, the change in the substances entering the reaction with time was found to be nonlinear. At first, ferrocene entered the reaction quickly, at this time its consumption was high, but as it progressed, its consumption in the reaction decreased. The high rate of obtaining the main products in the initial stage of the reaction occurred due to the rapid increase in the combination products. As the product of the compound increased, the amount of ferrocene entering the reaction decreased sharply in parallel. Very little of the ferrocene decomposed in the process for certain reasons.

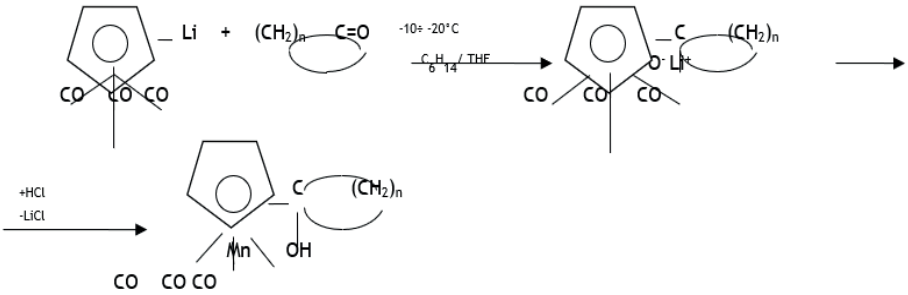
The derivative of simanthrene, simanthrene dimethylcarbinol, was obtained by reacting simanthrene with corresponding aliphatic ketones (acetone).



(4)

All the reactions considered were carried out in an interfacial catalytic environment. Analogously to ferrocene, the kinetic regularities of the reaction of symanthrene with acetone $(CH_3)_2CO$ were also studied.[10]

The reactions of ferrocene and symanthrene with cyclic ketones were also carried out. The reactions of symanthrene with cyclic ketones were carried out at lower temperatures than the reactions with ferrocene.



(5)

The yield of products obtained from the reactions of both ferrocene and cymanthrene with

cyclic ketones was very small compared to aliphatic ketones. This depends on many factors; reaction temperature, number of active collisions of molecules, steric factors, etc. The obtained metal organic complexes have antiknock properties and have been widely used in various brands of gasoline.[11,12]

The structure of cyclocarbinols obtained from the reactions of ferrocene and cymanthrene with cyclic ketones (cyclopentane and cyclohexane) was studied. IR spectra were recorded on a Specord M80 device based on ferrocene and cymanthrene.

As can be seen from figure 1, the valence absorption frequency of the C=O group of cyclopentanone, which was taken for the preparation of new derivatives of ferrocene with cyclic ketones, was $\nu_{c=o}$ 1680 cm^{-1} according to IR spectroscopy (Specord M80), and that of cyclohexanone was $\nu_{c=o}$1690 cm^{-1}. After the reaction, no signals corresponding to these groups were observed in the spectrum. This is explained by the transition of the ketone group (C=O) to the hydroxyl (OH) group. Based on the IR spectroscopy of ferrocene organometallic derivatives obtained with cyclopentanone and cyclohexanone, signals corresponding to OH groups were obtained in the region of 3420-3480 cm^{-1} for ferrocenylcyclopentanol, and in the region of 3450-3510 cm^{-1} for ferrocenylcyclohexanol.[13] Thus, for ferrocenylcyclopentanol (a) and ferrocenylcyclohexanol (b), the valence absorption frequencies ν_{OH} 3448 cm^{-1} and ν_{OH} 3468 cm^{-1} were obtained, respectively. These groups did not interact with the central atom either intramolecularly or intermolecularly.

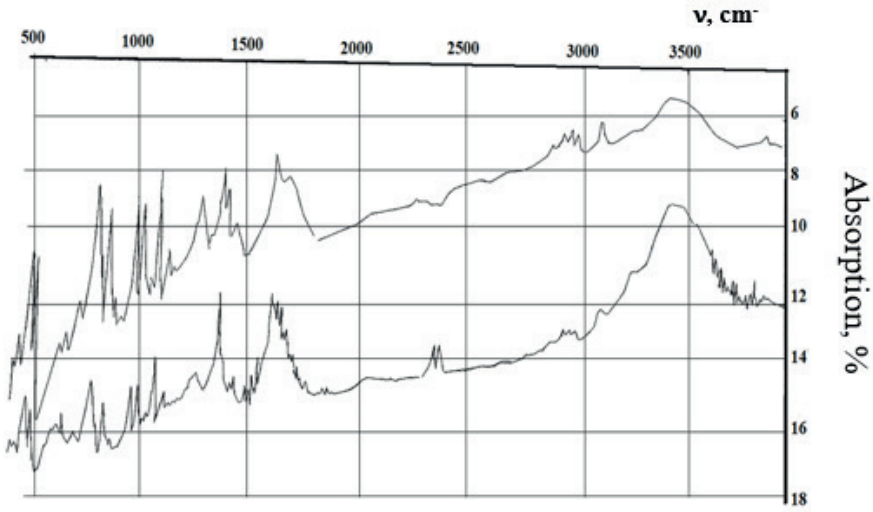


Figure 1. IR spectrum of ferrocenylcyclopentanol and ferrocenylcyclohexanol

Then, simantrenylcyclopentanol obtained by the same method was also analyzed by IR spectroscopy. The spectra were recorded in vaseline oil. No vibrational frequencies belonging to the ketone (CO) group were observed in the compound obtained as a result of the reaction. This suggests that the cyclic ketone taken as the initial reagent was used to obtain the corresponding carbinol. When analogous reactions were carried out with aliphatic ketones, no vibrational frequencies belonging to the CO-ketone group were observed in the end.[14]

As can be seen from figure 2, a valence absorption frequency of $\nu_{c=o}$ 3415 cm^{-1} was observed for the hydroxyl group. The valence absorption frequency of the CO group, located in the region

of $\nu_{c=o}$ 1938-2048 cm^{-1}, indicates the absence of intramolecular interaction between the C=O and OH groups.

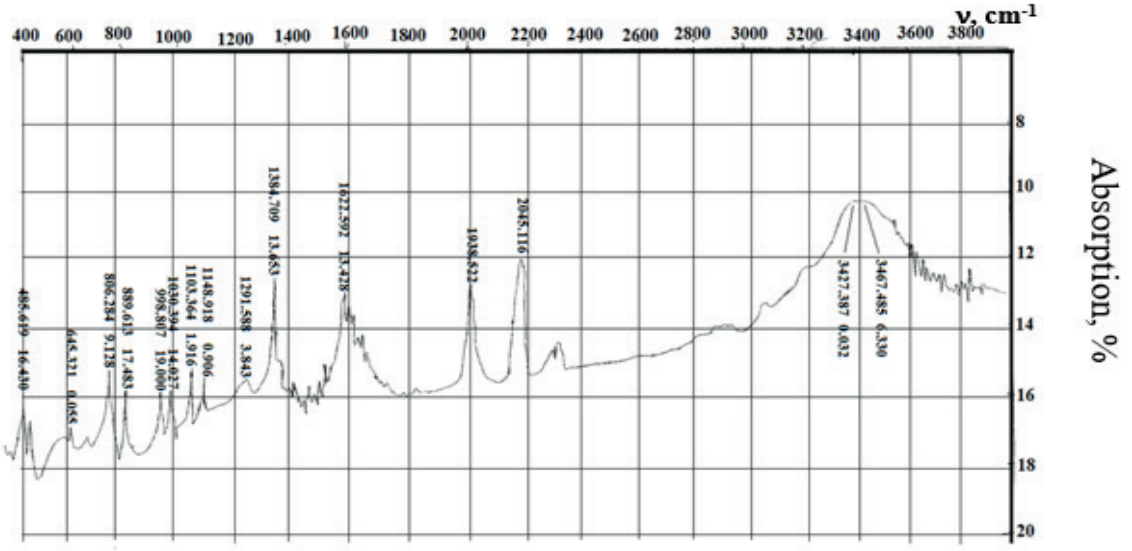
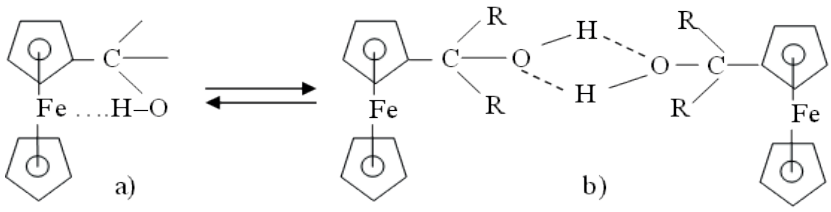


Figure 2. IR spectrum of simantrenylcyclopentanol



H^1NMR analyses were performed on a Bruker instrument. The spectrum was recorded at a temperature of C_4D_8O, 22^0 C. In the H^1NMR spectrum, a chemical shift of the field for the -OH group in the ferrocene molecule occurred from 2 m.h to 4,30 m.h. In the unsubstituted ferrocene molecule, the chemical shift of the protons in the cyclopentadiene (C_5H_5) ring (ligand) occurred at a field of δC_5H_5=4,12 parts per million. Due to the symmetry breaking after substitution, the cyclopentadiene ligand (C_5H_4) underwent cross-linking in the α and β positions and the protons became more mobile. For protons, chemical shifts occurred at 3,82 and 3,91 m.h. of the field. This is explained by the fact that the substituent group is a strong electron donor. This phenomenon occurred every time a substitution occurred in one of the cyclopentadiene ligands in the ferrocene core. It should be noted that depending on the difference in functional groups in the molecule, chemical shifts may differ slightly, but this difference in chemical shift is not very noticeable.[15,16,17]

The reactions considered with ferrocene proceeded mainly in an acidic medium. As a rule, these reactions do not proceed in an alkaline medium. It was found that the C-H acidity number of 10-11 in the ferrocene molecule does not affect the proton in its molecule, in this case the proton does not become mobile and, as a result, reactions with ketones do not occur. When the C-H acidity number is above 25, protonation of carbinol groups is ensured and the

reaction proceeds precisely at this time. In this regard, reactions with ferrocene must occur in an environment with a high pH. For the reaction to proceed, it was possible to increase the pH of the environment to 28-30. For this purpose, a strong acid - sulfuric acid - was used in all the reactions considered. Interestingly, when sulfuric acid was replaced with concentrated hydrochloric and phosphoric acids, the reaction did not occur. In the presence of concentrated hydrochloric and phosphoric acids, the molecule of the organometallic compound disintegrates and the reaction does not occur.

CONCLUSIONS

In the reviewed article, the reactions of ferrocene and cymanthrene with cyclic ketones were studied analogously to aliphatic ketones. Metal complex derivatives were obtained in lower yields from the interaction of the corresponding metallocenes with cyclopentanone and cyclohexanone compared to aliphatic ketones. In order to increase the yield, an interfacial catalysis environment was used. The yield of reaction products was relatively higher in the DEAN environment. 92 % concentrated sulfuric acid was used in the process. Reactions with cymanthrene were more difficult compared to ferrocene. Structural analysis of the obtained ferrocenyl- and cymanthreneylcyclocarbinols was carried out. Their structures were studied by IR spectroscopy and NMR method. IR spectroscopy was studied on a Spekord M80 device, and NMR analysis was studied on Bruker devices.

BIBLIOGRAPHIC REFERENCES

1. Hajiyeva SR, Gadirova EM. Electrophilic reactions of organometallic compounds in the presence of diethylammonium naphthenate. Baku Univ News. 2015;(4):42-5.

2. Hajiyeva SR, Rzayeva AR, Gadirova EM, et al. Synthesis of bis-ferrocenyl- and bis-cymanthrenyl isopropylate barium dihydrate metal complexes and study of their smoke-reducing properties. Chem Probl. 2010;(2):313-5.

3. Veliyev RA, Gadirova EM, Suleymanov GZ. Development of new methods for obtaining α-hydroxyisopropylferrocene and α-hydroxyisopropylsymantrene. Azerbaijan Chem J. 2010;(3):94-6.

4. Imanov EV, Mammadbayli EH, Gadirova EM, Abbasov MF, Suleymanova IH. Synthesis of 1-ferrocenylcyclohexan-1-ol by interfacial catalysis. In: Materials of the Republican Scientific Conference dedicated to the 90th anniversary of BSU; 2009; Baku. p. 121-2.

5. Imanov EV, Mammadbayli EH, Suleymanov GZ. Study of the reactivity, smoke reduction and demercaptation properties of ferrocene (cymanthrenyl) cyclopentyl (hexyl) carbinols and some of their derivatives in diesel fuels. Chem Probl. 2012;(2):39-47.

6. Hajiyeva SR, Gadirova EM. Analysis of factors affecting the interaction of ferrocene with cyclopentanone and cyclohexanone. Baku Univ News. 2014;(1):13-6.

7. Veliyev RA, Gadirova EM, Aliyev AM, et al. Synthesis of ferrocenyldimethylcarbinol under the conditions of interphase catalysis and study of kinetic regularities of the process. Rep ANAS. 2009;(4):97-101.

8. Suleymanov GZ, et al. Cyclic carbinol derivatives of ferrocene and cimantrene. Actual Probl Humanit Nat Sci. 2012;(8):22-6.

9. Gadirova EM, Veliyev RA, Suleymanov GZ, Efendi AJ. Kinetic study of the reaction of oxyalkylation of ferrocene and cymanthrene with acetone. In: Materials of the V Republican scientific conference of doctoral students, masters and young researchers dedicated to the 88th anniversary of the birth of the national leader Heydar Aliyev; 2011; Baku. p. 55.

10. Borisov YuA, Ustynyuk NA. Study of protonation of ferrocene. Izv RAN Ser Chem. 2002;(10):1749-56.

11. Suleymanov GZ, Mamedov ESh, Rustamova AI, et al. Ecologically clean anti-detonation fuel compositions prepared on the basis of alkyl and oxyalkyl derivatives of ferrocene and their solubility in various brands of gasoline and in their components. Izv Vuzov RF Khim Khim Tekhnol. 2007;50(5):82-5.

12. Suleymanov GZ, Litvishkov YN, Gadirova EM, et al. Features and anti-detonation efficiency of compositions prepared on the basis of new mono- and binuclear alkyl and oxyalkyl derivatives of ferrocene and cimanthrene. Izv Vuzov RF Khim Khim Tekhnol. 2005;48(12):73-7.

13. Suleymanov GZ, Tahirli NM, Suleymanova IH, Gadirova EM. Interaction reaction of ferrocene with cyclohexanone using a two-phase catalytic system. In: Scientific conference dedicated to the 88th anniversary of the birth of H.A. Aliyev; 2011; Baku. p. 57.

14. Imanov EH. Synthesis, structure and properties of cyclopentanol, cyclohexanol derivatives of ferrocene and cymanthrene. Baku; 2013. 25 p.

15. Gadirova EM, Veliyev RA, Suleymanov GZ. Study of the reaction of ferrocenyl- and cymanthrenyl-carbinol metal complexes in interfacial catalytic environment. In: Materials of the Republican scientific conference "Organic reagents in analytical chemistry" dedicated to the 95th anniversary of Professor A.A. Verdizade; 2009; Baku. p. 33-4.

16. Gadirova EM, Veliyev RA, Suleymanov GZ, Efendi AJ. Kinetic study of the reaction of oxyalkylation of ferrocene and cymanthren with acetone. In: Materials of the V Republican scientific conference of doctoral students, masters and young researchers dedicated to the 88th anniversary of the birth of the national leader Heydar Aliyev; 2011; Baku. p. 55.

17. Gadirova EM. Synthesis of thioether derivatives of ferrocenylcarbinols. Baku Univ News. 2013;(3):45-8.

FINANCING

None.

CONFLICT OF INTEREST

None.

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