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ORGANIC MAGNESIUM COMPOUNDS SYNTHESIS OF AROMATIC ACETYLENE ALCOHOLS

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ОРГАНИЧЕСКОЕ МАГНИЕВОЕ СОЕДИНЕНИЕ СИНТЕЗ АРОМАТИЧЕСКИХ АЦЕТИЛЕНОВЫХ СПИРТОВ

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ABSTRACT

Aromatic acetylenic alcohols (AAA) were synthesized as a result of the reaction of methyl propyl ketone, diethyl ketone, methyl isopropyl ketone and pinocoline with phenylacetylene in the presence of a Grignard reagent. The effect of DEE and THF solvents on the product yield was studied. It was determined that the average yield of AAA is 11.0 % higher in THF than DEE.

АННОТАЦИЯ

В результате реакции метилпропилкетона, диэтилкетона, метилизопропилкетона и пиноколина с фенилацетиленом с реактивом Гриньяра синтезированы ароматические ацетиленовые спирты (ААС). Изучено влияние на выход продукта растворителей ДЭЭ и ТГФ. Определено, что выход ААС в средном на 11,0% больше в растворителе ТГФ, чем ДЭЭ.

Keywords: ketones, methylpropyl ketone, diethyl ketone, methyl isopropyl ketone, pinocoline, phenylacetylene, organic magnesium, phenylacetylene, aromatic asetylenic alcohols.

Ключевые слова: кетоны, метилпропилкетон, диэтилкетон, метилизопропилкетон, пиноколин, фенилацетилен, магний органическое соединение, фенилацетилен, ароматические ацетиленовые спирты.

Introduction. The role of elemental organic compounds is important in organic chemistry. Currently, in organic synthesis, various new compounds are being synthesized based on elemental organic compounds.

Metal organic compounds were first synthesized by A.D. Franklin in 1849 [1]. In 1829 Sh.R. Barbe synthesized mixed metal organic compounds [2]. The French scientist V.M. Grignard synthesized mixed magnesium organic compounds (Grignard’s reagent) by reacting powdered magnesium metal to a solution of alkyl halides in dehydrated ether (Iotsich reagent) [3-4]. Based on this, it is called the Grignard-Iotsich method [5].

Organometallic reagents are often used in the synthesis of organic molecules because they promote the formation of certain bonds and (or) catalyze the reaction. Individual reactions are difficult or impractical to carry out otherwise. In most organic compounds, the carbon atoms are electrophilic, but in organometallic compounds, the metal atom usually has less electronegativity than its bonded carbon atom, so the carbon becomes nucleophilic with varying strength. When a metal with high electronegativity is used, the charge distribution increases the intensity of its ionic properties and the reactivity of the compound [6-7]. New stable compounds were synthesized by Iotsich on the basis of reaction of Grignard's reagent with alkynes [8-10].

In this research work, aromatic acetylene alcohols (AAA) were synthesized based on the methods presented in the literature. In order to determine the range of relative efficiency of the synthesized

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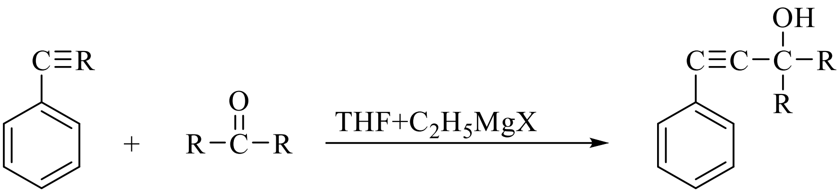
compounds, their reactions based on organic metal compounds were also studied. Studies were conducted on the process of synthesis of AAA on the basis of organic magnesium compounds used on a large scale in organic synthesis, according to the Grignard-Iotsich reaction. Based on the reaction of ketones - methylpropylketone, diethylketone, methylisopropylketone, pinokalins- with magnesium organic compounds based on Grignard-Iotsich reaction, corresponding AAA was synthesized. The reaction equation was proposed as follows.



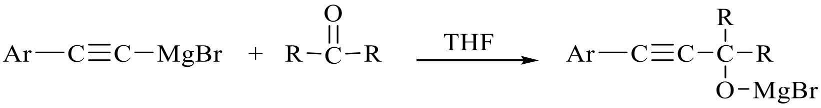
Here it is: R = -CH_3, -C_2H_5, -C_3H_7, iso- C_3H_7
X = halogen

Reaction to obtain aromatic acetylic alcohols

The formation of the iodine complex is due to the active hydrogen in phenylacetylene. In this case, phenylacetene was added dropping to a solution of ethylene ethyl magnesium bromide (Grignard's reagent) in TGF, and the magnesium bromide derivative of phenyl acetylene (Iotsich's reagent) was prepared.

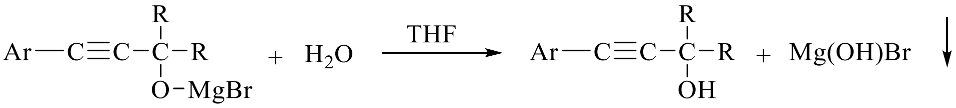
$$Ar-C\equiv CH + C_2H_5MgBr \xrightarrow{THF} Ar-C\equiv C-MgBr + C_2H_6\uparrow$$

The resulting Iotsich reagent reacts with ketones to form intermediate AAA metal halide salts.



$$Ar-C\equiv C-MgBr + R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{THF} Ar-C\equiv C-\overset{R}{\underset{O-MgBr}{C}}-R$$

AAA was formed when the resulting substance was hydrolyzed in ice water.



$$Ar-C\equiv C-\overset{R}{\underset{O-MgBr}{C}}-R + H_2O \xrightarrow{THF} Ar-C\equiv C-\overset{R}{\underset{OH}{C}}-R + Mg(OH)Br\downarrow$$

Experimental part. A sieve, a reflux condenser, a thermometer and a dropping funnel are installed in a four-necked flask and 75 ml of absolute tetrahydrofuran and 3.05 g (0.125 mol) of powdered magnesium metal are mixed in it. Then, through the dropping funnel, 19.0 g of ethyl bromide and equal amount of tetrahydrofuran mixture is added. The reaction mixture is boiled vigorously for 50-55 minutes. The resulting product (Grignar reagent) was cooled to room temperature (25-27 ºC) and stirred for another 60 minutes.

12.5 g (0.125 mol) of phenylacetylene is dripped with stirring to the Grignard reagent solution formed as a result of the reaction for 2 hours (the temperature of -5-0ºC in the flask is created by liquid nitrogen), then an equal amount of absolute ether solution of 0.25 mol of ketones is added to it over 2 hours. Upon completion of the reaction, the resulting mixture (3x25 ml) was hydrolyzed with ice water and diluted hydrochloric acid was added until the precipitate dissolved. After separating the part of organic substances, the aqueous part is extracted again (3x25 ml). The extract is dried with sodium sulfate or potash, the diethyl ether is driven off under normal conditions, and the remainder is fractionated by driving under vacuum.

Research results and analysis. Depending on the structure of the selected ketones, different AAA are formed as a result of the reaction with phenylacetylene. Including 25.5 g (0.25 mol) of phenylacetylene and 21.5 g (0.25 mol) of methylpropylketone 3-methyl-1-phenylhexin-1-ol-3 (1) (80.0 %) nD 1.5126, d_2=1.1261 g/cm^3; Using 25.5 g (0.25 mol) of phenylacetylene and 21.5 g (0.25 mol) of diethyl ketone, 3-ethyl-1-phenylpentin-1-ol-3 (2) (79.3 %), nD=1,5333, d_2=1.0765 g/cm^3 ; 25.5 g (0.25 mol) of phenylacetylene and 21.5 g (0.25 mol) of 3,4-dimethyl-1-phenylpentin-1-ol-3 using isopropyl ketone (3) (76.4%) p_2=1.5400, d_2=1.0010 g/cm^3; From the reaction of 25.5 g (0.25 mol) of phenylacetylene and 25.0 g (0.25 mol) of pinokalin, 3,4,4-trimethyl-1-phenylpentin-1-ol-3 (4) (72.1 %), n™ = 1.5360, d_2 =1.9223 g/cm^3 were synthesized.

The process of synthesis of AAA by Grignard-Iotsich method was carried out for 2-6 hours in a temperature range of -5 -10ºC. Starting products were obtained in equimolar proportions.

Table 1.

Influence of nature of solvents and duration of reaction on AAA yield (temperature -5-0°C)

Synthesized AAA	**Product yield, %**	
	Solvent DEE	**Solvent TGF**
Duration of reaction, 2 hours		
1	64.4	82.0
2	61.3	76.0
3	56.4	74.5
4	53.0	69.3
Duration of reaction, 4 hours		
1	71.4	80.0
2	66.4	79.3
3	61.3	76.4
4	57.3	72.1
Duration of reaction, 6 hours		
1	57.0	73.0
2	54.8	71.3
3	52.4	69.5
4	45.2	63.2

As can be seen from the table, compared to DEE, when the process was carried out in TGF solution, a higher yield of AAA was synthesized, in addition, the expected product yield peak was observed as the reaction time increased from 2 to 4 hours. In order to find the most alternative conditions for the reaction, it was found that the efficiency of the AAA decreased sharply when the research was carried out for 6 hours. It was found that the nature and structure of the radicals in the ketone molecule also affect the yield of the product.

We can explain the effect of reaction duration and nature of solvent on AAA yield as follows.

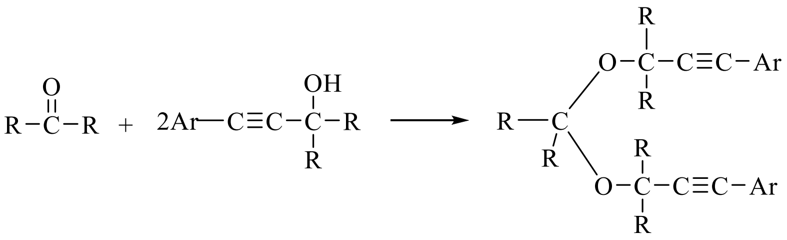
The highest III- 80.0 when the duration of the reaction in TGF solution is carried out in 4 hours; 2 - 79.3; 3 - 76.4 %; 4 - 72.1 %; successfully synthesized.

When the process was carried out for 2 hours, it was observed that ketones that could not react completely were condensed or enolized to form stable intermediates and adducts.

As a result of enolization of straight chain ketones, 8 protons are released first under the influence of an oxonium type salt, then under the influence of water, and enol is directly formed in the reaction.

In a weak alkaline environment, that is, in enolization reactions, enol occurs through the step of enolate-anion formation. Due to the addition of a hydrogen ion to the oxygen of the carbonyl group, the separation of the proton from the carbon atom in the intermediate compound formed in the process is accelerated. Because the positively charged oxygen atom (>C=$^{+}$OH) strongly attracts electron clouds, proton release becomes easier.

When the Grignard-Iotsich reaction is carried out for 6 hours, it should be recognized that the yield of the product decreases according to the same law in the selected solvents. In this case, the AAA produced in the process interacts with unreacted ketones to form acetals, AAA partially polymerizes, or reacts with Mg (OH)Br in the solution and turns into alcohols, resulting in a decrease in product yield.

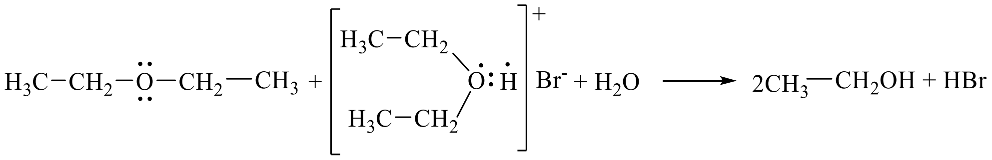


Based on the results of the conducted research, it was proposed that the process for the synthesis of AAA by the Grignard-Iotsich method was carried out in 4 hours as the most effective.

As can be seen from the table, the reaction was carried out in solutions of DEE and TGF, when the process was carried out in solution of TGF, AAA was produced in high yield. For example, when the reaction is carried out in DEE at a temperature of -5 - 0 ºC in 4 hours, AAA 1 - 71.4 %; 2 - 66.4 %; 3 - 61.3 %; 4 - with 57.3 %, and in TGF - 80.0, respectively; 78.2; 75.2; 71.0 % yield, i.e. 11.0 % high selectivity on average was observed. It was found that the reason for this is that when magnesium metal reacts with alkyl halide in DEE solution, the reaction is very slow, and in TGF solution, the process is very fast and a large amount of Grignard’s reagent is formed. The oxygen atom in DEE has a basic property due to its non-generalized electron pair, and in TGF, due to the strong delocalization of the negative charge in the ring, it has a very strong basic property, so it solvates the cationic part of the Grinard reagent, that is, the acid part. In addition, these solvents are not only solvents; they also act as catalysts at the same time. In catalytic reactions, it is known that catalysts with high basicity have high catalytic activity, which serves to increase product yield.

The positively charged hydrogen ion of the acid and water formed in small amounts in the DEE system combines with one free electron in the ether oxygen to form an oxonium ion. Oxonium ion undergoes easy hydrolysis under the influence of water and turns into ethanol.

Ethanol, as a result of absorbing magnesium metal from the solution, turns into a stable, more difficult-to-dissolve alcohol. This, in turn, leads to a decrease in the amount of water that hydrolyzes AAA halogen salts, which are formed as an intermediate product in the reaction, as a result, the product yield decreases, and the appearance of additional substances increases.



$$H_3C-CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2-CH_3+\left[\begin{array}{l}H_3C-CH_2\\ \qquad\qquad\ddot{O}\!:\!H\\ H_3C-CH_2\end{array}\right]^{+}Br^{-}+H_2O\longrightarrow 2CH_3-CH_2OH+HBr$$

When the reaction is carried out in TGF, intermediate and by-products are formed in small quantities, the solubility of the Iotsich reagent in TGF solution is very high, creating a favorable environment for its spatial collision with ketones. During the hydrolysis of the AAA halogen salt formed in the process, TGF acts as a catalyst, and the unshared electron pair in its molecule helps to solvate the salt and quickly turn it into AAA. TGF is less soluble in water in the system compared to DEE, in a weakly acidic environment it forms by-products such as tetramethylene glycol, which is unstable with water, and tetramethylenechlorohydrin with acid. The byproducts react with magnesium hydrobromide dissolved in the synthesized AAA to form an intermediate, which reduces the amount of formation of alcohols with the base salt of the AAA, allowing for the high-yield synthesis of alcohols.

When the Grignard-Iotsich reaction was carried out in solutions of DEE and TGF, which are aprotic solvents, it was proved that the product yield was higher in TGF, which has a higher dielectric constant and dipole moment.

It can be seen from table 1 that when AAA is synthesized on the basis of organometallic compounds, the molecular mass of the starting products (ketones), the structure, and the nature of the radicals affect the product yield. The obtained results show that the increase in the molecular mass of ketones or the increase in bulky radicals around the carbonyl group complicates the process. In acetone, which has a symmetrical structure, the density of electron clouds around the carbonyl group is evenly distributed and it is a polar molecule. The location of various radicals around the carbonyl group weakens its spatial movement, which causes the reaction of methylpropylketone, methylisopropylketone and methyltertiarybutylketone with the Iotsich reagent to be somewhat difficult due to the negative impact on the active center.

According to the nature of the radicals located around the carbon of the carbonyl group and the property of spatial interaction of the radicals, it was determined that the initiation of ketones into the Grignard-Iotsich reaction increases in the following order - pinokalin < methylisopropylketone < diethylketone < methylpropylketone.

The process of synthesis of AAA by the Grignard-Iotsich method was carried out for 4 hours in an equimolar ratio of initial products, in TGF solution, at a temperature of -5-0 ^{o}C and was chosen as the most alternative condition.

The purity of the synthesized AAA was studied by chromatographic methods, its structure was studied by IR and NMR spectroscopic methods, and its elemental composition was analyzed.

In the IQ spectrum of 3-ethyl-1-phenylpentin-1-ol-3 following areas of absorption were observed: at 3400 - 3500 cm^{-1} molecule valence vibration of the -OH group, at 2934 cm^{-1} and 2972 cm^{-1}. Symmetric and asymmetric valence vibrations of $-CH_2-$, $-CH_3$ groups correspond to the valence vibration 1957 - 1880 cm^{-1} of the -C=C- group. At 1685-1615 cm^{-1}, the vibration of the -C=C- bond in the aromatic ring was observed.

The following resonance frequencies were observed in the NMR spectrum of 3-ethyl-1-phenylpentin-1-ol-3. A triplet signal appears in the field of 0.9 ppm and is a signal of protons of the $-CH_3$ group connected with $-CH_2-$. At 1.1 ppm singlet signals appear, proton signals of the $-C-CH_3$ group. 2.5 - 2.7 ppm. A quartet signal appears between $-CH_3$ and $-CH_2$ - protons. 5.7-5.9 ppm. The signal of the -OH group in the singlet signal of the molecule is H_2, H_6 at 7.3-7.6 ppm and the signals of H_3, H_4, H_5 protons in the range of 7.0-7.2 were observed.

Conclusions

AAA was synthesized cunducting reaction of phenylacetylene of methylpropylketone, dimethylketone, methylisopropylketone and pinocholines with organic magnesium compound. The effects of DEE and TGF solvents on the yield of the reaction were studied and it was found that AAA was formed with higher yield when the process was carried out in TGF solution. When the reaction is carried out at the temperature of -5-0 ^{o}C in 4 hours; AAA 1 - 71.4 %, 2 - 65.2 %; 3 - 60.6 %; 4 - with 55.9 %, and 80.0 in TGF, respectively; 78.2; 75.2; 71.0 % yield, i.e. 11.0% high selectivity on average was observed. It was noted that the participation of ketones in the Grignard-Iotsich reaction increases in the following order – pinokalin < methylisopropylketone < diethylketone < methylpropylketone.

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