

SYNTHESIS OF TERTIARY ALCOHOLS BASED ON ORGANIC MAGNESIUM COMPOUNDS

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Abstract

The reaction of organomagnesium compounds with thiochromane series acyl derivatives was studied. As a result of the reaction, it was found that thiochroman acyl derivatives react with organomagnesium compounds like aliphatic and aromatic ketones and form the corresponding tertiary alcohols with high yield.

Keywords: magnesium, tertiary alcohol, absolute ether, charge, reagent. thiochroman, acylthiochroman, organomagnesium compound, nucleophile, carbonyl group, ketone,

INTRODUCTION

In organomagnesium compounds, the magnesium atom is directly bonded to the carbon atom of the organic compound. The electronegativity difference between atoms in this bond is quite large. Therefore, the bond between carbon and magnesium in mixed organomagnesium compounds is strongly polarized. A partial negative charge appears on the carbon atom bonded to magnesium in the molecule. It can be seen that organomagnesium compounds are considered nucleophilic reagents and participate in the reaction as an agent exhibiting high reactivity for compounds with a positively charged reaction center.

MATERIALS AND METHODS

Based on magnesium organic compounds general method of synthesis of tertiary alcohols

The reaction of thiochromane acyl derivatives with organomagnesium compounds was studied to study chemical changes. 6-acetyl-1-thiochromene and various alkyl halides were used in the reaction.

Synthesis of 6-(1-methyl-1-oxopropyl)-1-thiochroman (I)

In a 250 ml three-necked flask equipped with a mechanical stirrer, an inverted condenser and a dropping funnel, we add 1 g of magnesium powder and 10 ml of absolute ether. We slowly heat the flask to a temperature of 25 °C in a water bath. Add 3 ml of propyl bromide dropwise through the dropping funnel to the heated flask over 10 minutes. In this case, the reaction mixture must be constantly stirred. After that, we keep the reaction flask for 2 hours at a temperature of 40-45 °C with stirring. The completion of the reaction can be known from the complete reaction of the magnesium powder in the flask. Then cool the reaction flask from the outside with ice and dropwise add 2 g of 6-acetyl-1-thiochroman dissolved in 10 ml of absolute ether to the reaction flask through the dropping

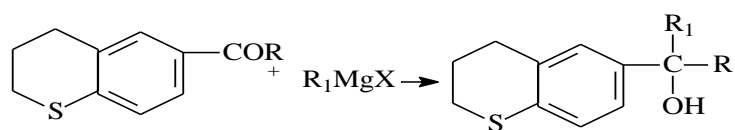
funnel. Initially, a white precipitate appears during the dropwise process of 6-acetyl-1-thiochroman, which dissolves in the ether in the reaction flask. By the end of the reaction, this white precipitate turns into a soft mass. In order to complete the reaction, the reaction flask is heated in a water bath for 30 minutes. The reaction flask is cooled externally and the product is decomposed using ammonium chloride solution. After that, two different transparent layers are formed in the reaction flask. The ether layer is separated using a separatory funnel. The aqueous layer is extracted several times with pure ether. All ethereal solutions are combined, washed with cold water and dried with potash. After that, the solvent (ether) is removed, the purity and individuality of the substance is checked in the benzene:hexane (1:4) system using a "silufol" plate. The yield of the product, namely 6-(1-methyl-1-oxypropyl)-1-thiochroman, was 1.85 g or 80%. The refractive index was found to be $n_D^{20} = 1.59100$. Element analysis: Found, %: S 70.53; N 8.30. Calculated for the formula $C_{13}H_{18}OS$, %: C 70.30; N 8,10

Synthesis of 6-(1-methyl-1-oxybutyl)-1-thiochroman (II)

The synthesis of this substance was carried out by the method described above for the synthesis of 6-(1-methyl-1-oxypropyl)-1-thiochroman (I). For the reaction, 1 g of magnesium powder, 10 ml of absolute ether, 3 ml of propyl bromide, 2 g of 6-acetyl-1-thiochromans dissolved in 10 ml of absolute ether were taken. The yield of the product, namely 6-(1-methyl-1-oxybutyl)-1-thiochroman, was 2.06 g or 84%. The refractive index was found to be $n_D^{20} = 1.56930$. Element analysis: Found, %: S 71.27; N 8.57. Calculated for the formula $C_{14}H_{20}OS$, %: C 71.18; N 8.47.

RESULTS

It is known that the reaction of organomagnesium compounds with ketones is one of the main ways of obtaining tertiary alcohols. For this, a reaction was carried out in magnesium powder and absolute ether. The synthesis process carried out above can be expressed schematically on the basis of the following chemical formulas:



I. $R=CH_3$; $R_1= C_2H_5$; II. $R=CH_3$; $R_1= C_3H_7$;

During the conducted reaction, it was found that the reaction yield of acylthiochromans is high. Thus, it was shown that radical compounds with a high number of carbon atoms in the hydrocarbon radical are much superior in terms of their ability to react in the reaction of acylthiochromans with organomagnesium compounds. All of the resulting compounds are viscous solid-liquid substances, and the following tables provide information on the physicochemical classifications and elemental analyzes of the obtained compounds.

Thiochromane series of tertiary alcohols physicochemical description Table.1

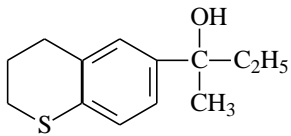
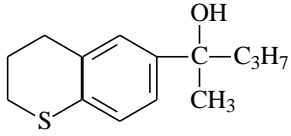
O/n	Percentage, %	n ²⁰ _D	Found, %.		Gross формула	Calculated, %.		R	R ₁
			C	H		C	H		
I	80	1,5910	70,75 70,53	8,49 8,30	C ₁₃ H ₁₈ OS	70,30	8,10	CH ₃	C ₂ H ₅
II	84	1,5693	71,35 71,27	8,60 8,57	C ₁₄ H ₂₀ OS	71,18	8,47	CH ₃	C ₃ H ₇

The structure of the synthesized compounds was confirmed using IR- and PMR-spectroscopic methods calculated from modern research methods. The progress of the reaction was monitored by thin-layer chromatography. The purity of the obtained substances and its identification was carried out using a "silufol" plate in the benzene-hexane (1:5) system.

When the IR-spectrum of the synthesized compounds was compared with the IR-spectra of the original acylthiochroman molecules, it became clear that the absorption lines in the 1700 cm⁻¹ region characteristic of the carbonyl group in the IR-spectrum of the original substance were completely absent in the IR-spectra of the formed tertiary alcohols. Instead, it was found that new absorption lines characteristic of the OH group appeared in the region of 3400 cm⁻¹.

The following tables present the data related to the PMR-spectrum expressed as HO-C(A)(B) of the synthesized thiochromane tertiary alcohols.

Thiochromane series of tertiary alcohols PMR-spectrum information Table 2

Compound Number	Structural formula	Substituents, chemical shift (m.h.)		
		OH	A	B
XX		2,70	1,50	CH ₃ 0,90 CH ₂ 1,60
XXI		2,56	1,49	CH ₃ 0,90 CH ₂ 1,65 (4 proton)

Note: here R- should be considered as a fragment of thiochromene molecule.

In the PMR spectrum of the 6-Acetyl-1-thiochroman molecule, the signals of the protons of the methyl group belonging to the carbonyl group are in the singlet form at 2.6 m.h., while the signals of the protons of the CH₂ group attached to the aromatic ring in the heteroring are in the form of a tilted triplet at 1.78 m.h., is observed. The signals of the other CH₂ groups of the ring appear similarly to the above at 2.52 m.h., and 2.79 m.h., and 6.34 m.h. Protons of CH groups in the aromatic ring are 7.38 m.h., 7.49 m.h. and appears at 6.84 m.h. The constant of spin-spin interactions between methylene groups is equal to 6 Hz. The constant of spin-spin interactions of aromatic ring protons is JH₅H₇ = 7 Hz, JH₇H₈ = 29 Hz

[1; P.82-86, 2; P. 20 22].

CONCLUSION

As a result of studying the reaction of obtaining tertiary alcohols on the basis of organomagnesium compounds, it was found that the yield of the reaction product increases in parallel with the increase in the mass of the reactant. The resulting thiochroman series of tertiary alcohols are soluble in organic solvents, have a characteristic pleasant smell and are bright reddish colored substances. Thus, in conclusion, it can be said that thiochromane series acyl derivatives behave like aliphatic and aromatic ketones in reactions with organomagnesium compounds and form their corresponding tertiary alcohols with high yield.

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