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ON THE BASIS OF THIOCHROMAN ATSIL COMPOUND SYNTHESIS OF TRIAL ALCOHOLS

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Abstract. The reaction of thiochroman series acyl derivatives with magnesium organic compounds was studied. As a result of the reaction, it was found that thiochroman acyl derivatives react with magnesium compounds, such as aliphatic and aromatic ketones, to form tertiary alcohols corresponding to high yields.

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

INTRODUCTION

As we all know, in magnesium compounds, the magnesium atom is directly bound to the carbon atom of the organic compound. The difference in inter-atomic electromagnetism in this bond is quite large. Therefore, the bond between carbon and magnesium in mixed magnesium compounds is strongly polarized. A partially negative charge is formed on the carbon atom attached to the magnesium in the molecule. It can be seen that magnesium organic compounds are nucleophilic reagents and are agents that exhibit high reactivity for positively charged reaction-centered compounds. Below, we have studied the chemical properties of acylthiochromans containing carbonyl groups in the synthesis of tertiary alcohols based on these magnesium compounds.

MATERIALS AND METODS

Based on thiochroman atsils a general method of synthesis of tertiary alcohols

The reaction of thiochroman alkaloids with magnesium-organic compounds has been studied to study chemical changes. 6-acetyl-1-thiochroman and various alkylgalagenides were used in the reaction.

6-(1-метил-1-оксипропил)-1-тиохроман синтези (I)

Equip a three-tube flask with a volume of 250 ml with a mechanical stirrer, an inverted refrigerator and a dropper funnel, add 1 g of magnesium scrap and 10 ml of absolute ether. Heat the flask slowly in a water bath to 25 ° C. Add 3 ml of propylbromide to the heated flask dropwise through the dropper funnel for 10 min. In this case, the reaction mixture must be constantly stirred. We then keep

the reaction flask at stirring for 40-45 ° C for 2 h. The completion of the reaction can be determined from the complete reaction of the magnesium scrap in the tube. Then cool the reaction flask with ice on the outside and add 2 g of 6 g acetyl-1-thiochroman dissolved in 10 ml of absolute ether to the reaction flask drop by drop through the dropper funnel. Initially, a white precipitate is formed during the instillation of 6-acetyl-1-thiochroman, and it dissolves in the ether in the reaction tube. By the end of the reaction, this white precipitate turns into a soft mass. To complete the reaction, the reaction tube is heated in a water bath for 30 minutes. The reaction tube is cooled on the outside and the resulting substance is decomposed using a solution of ammonium chloride. Two different transparent layers are then formed in the reaction tube. The ether layer is separated using a separating funnel. The aqueous layer is extracted several times with pure ether. All ether solutions are combined, washed in cold water and dried using a potash. The solvent (ether) is then expelled, and the purity and individuality of the substance are checked in a benzene: hexane (1: 4) system using a "silufol" plate. The yield of the product i.e. 6- (1-methyl-1-oxypropyl) -1-thiochroman is 1.85 g or 80%. The refractive index was found to be p20d = 1.59100. Element analysis: Found,%: S 70.53; N 8.30. Calculated for formula C13H18OS,%: S 70.30; N 8,10

6- (1-methyl-1-oxybutyl) -1-thiochroman synthesis (II)

Equip a three-tube flask with a volume of 250 ml with a mechanical stirrer, an inverted refrigerator and a dropper funnel, add 1 g of magnesium scrap and 10 ml of absolute ether. Heat the flask slowly in a water bath to 25 ° C. Add 3 ml of propylbromide to the heated flask dropwise through the dropper funnel for 10 min. In this case, the reaction mixture must be constantly stirred. We then keep the reaction flask at stirring for 40-45 ° C for 2 h. The completion of the reaction can be determined from the complete reaction of the magnesium scrap in the tube. Then cool the reaction flask with ice on the outside and add 2 g of 6 g acetyl-1-thiochroman dissolved in 10 ml of absolute ether to the reaction flask drop by drop through the dropper funnel. Initially, a white precipitate is formed during the instillation of 6-acetyl-1-thiochroman, and it dissolves in the ether in the reaction tube. By the end of the reaction, this white precipitate turns into a soft mass. To complete the reaction, the reaction tube is heated in a water bath for 30 minutes. The reaction tube is cooled on the outside and the resulting substance is decomposed using a solution of ammonium chloride. Two different transparent layers are then formed in the reaction tube. The ether layer is separated using a separating funnel. The aqueous layer is extracted several times with pure ether. All ether solutions are combined, washed in cold water and dried using a potash. The solvent (ether) is then expelled, and the purity and individuality of the substance are checked in a benzene: hexane (1: 4) system using a "silufol" plate. The yield of the product i.e. 6- (1-methyl-1-oxypropyl) -1-thiochroman is 1.85 g or 80%. The refractive index was found to be p20d = 1.59100. Element analysis: Found,%: S 70.53; N 8.30. Calculated for formula C13H18OS,%: S 70.30; N 8,10

6- (1-methyl-1-oxyamyl) -1-thiochroman synthesis (III)

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 shavings, 10 ml of absolute ether, 3 ml of butyl bromide, 2 g of 6-acetyl-1-thiochromones dissolved in 10 ml of absolute ether were obtained. The yield of the product i.e. 6- (1-methyl-1-oxyamyl) -1-thiochroman is 2.37 g

91%. The refractive index was found to be p20d = 1.57540. Element analysis: Found,%: S 72,16; N 9.00. Calculated for formula C15H22OS,%: S 71.95; N 8.85.

6- (1-ethyl-1-oxyamyl) -1-thiochroman synthesis (IV)

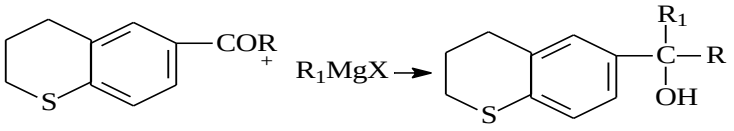
The synthesis of this substance was carried out by the method described above for the synthesis of 6-(1-methyl-1-oxypropyl) -1-thiochroman (I). For the reaction, 1 g of magnesium shavings, 10 ml of absolute ether, 3 ml of butyl bromide, 2 g of 6-propionyl-1-thiochromones dissolved in 10 ml of absolute ether were obtained. The yield of the product i.e. 6- (1-ethyl-1-oxyamyl) -1-thiochroman is 2.4 g or 93%. The refractive index was found to be p20d = 1.58290. Element analysis: Found,%: S 72.85; N 9,26. Calculated for formula C16H24OS,%: S 72.72; N 9,10.

6-Methyl-7- (1-methyl-1-oxypropyl) -1-thiochroman synthesis (V)

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 shavings, 10 ml of absolute ether, 3 ml of ethyl bromide, 2 g of 6-methyl-7-acetyl-1-thiochroman dissolved in 10 ml of absolute ether were obtained. The yield of the product i.e. 6-methyl-7- (1-methyl-1-oxypropyl) -1-thiochroman is 1.97 g or 86%. The refractive index was found to be p20d = 1.56700. Element analysis: Found,%: S 71,23; N 8.53. Calculated for formula C14H20OS,%: S 71.18; N 8,47.

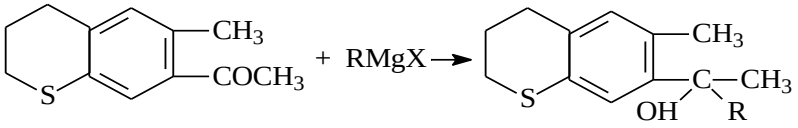
REZULTS (DISCUSSION)

It is known that the reaction of magnesium compounds with ketones serves as one of the main methods of obtaining tertiary alcohols. For this, a reaction was carried out on magnesium shavings and absolute ether. The above synthesis process can be schematically expressed 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 ;

III. R=CH_3; R_1= C_4H_9 ; IV. R= C_2H_5; R_1= C_4H_9 ;



V R= C_2H_5

During the reaction, it was found that the reaction yield of acetylchromanes was high. Hence, in the reaction of acylthiochromans with magnesium-organic compounds, radical compounds with a high number of carbon atoms in the hydrocarbon radical showed a significant advantage. All of the compounds obtained are viscous thick-liquid substances, and the following tables provide information on the physicochemical classifications of the compounds obtained and elemental analysis.

Thiochroman series tertiary alcohols

physicochemical characteristics

Table-1

s.n.	P %	$n^{20}_{д}$	Found %.		Brutto formula	Calculated, %.			
			C	H		C	H	R	R_1
I	80	1,5910	70,75 70,53	8,49 8,30	$C_{13}H_{18}OS$	70,30	8,10	CH_3	C_2H_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_3H_7
III	91	1,5754	72,21 72,16	9,12 9,00	$C_{15}H_{22}OS$	71,95	8,85	CH_3	C_4H_9
IV	93	1,5829	72,85 72,81	9,26 9,18	$C_{15}H_{22}OS$	72,72	9,10	C_2H_5	C_4H_9
V	86	1,5670	76,33 71,23	8,60 8,53	$C_{14}H_{20}OS$	71,18	8,47	C_2H_5	

The structure of the synthesized compounds was confirmed using IR- and PMRspectroscopic methods calculated from modern research methods. The course of the reaction was monitored using a thin-layer chromatographic method. 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 spectra of the synthesized compounds were compared with the IR spectra of the original acetylchromane molecules, it was found that the IR spectra of the tertiary alcohols formed in the 1700 cm-1 region characteristic of carbonyl grout in the IR spectrum of the original substance were completely absent. Instead, new absorption lines specific to the ON group appeared in the 3400 cm-1 area.

The following tables provide data relating to the PMR spectrum of synthesized thiochroman ternary alcohols expressed in the form NO-S (A) (V).

Thiochroman series tertiary alcohols

PMR-spectrum data

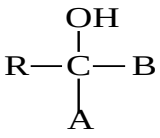
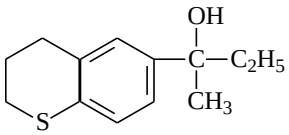
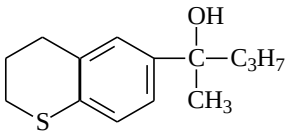
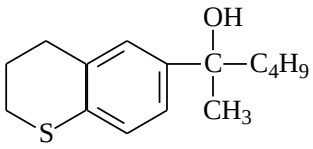
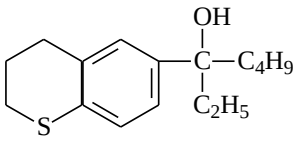
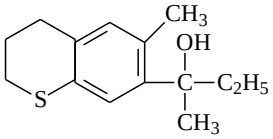


Table -2

Connection number	Structure formula	Substitutes, chemical shift (м.sh.)		
		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 protons)
XXII		2,95	1,48	CH_3 0,88 CH_2 1,30 (6 protons)
XXIII		2,64	CH_3 0,90 CH_2 1,61	CH_3 0,88 CH_2 1,30 (6 protons)
XXIV		2,70	1,50	CH_3 0,90 CH_2 1,61

Note: Let R be considered here as a fragment of the thiochroman molecule.

In the PMR spectrum of the 6-acetyl-1-thiochroman molecule, the signals of protons of the methyl group belonging to the carbonyl group are observed in singlet form at 2.6 m.h. m.h., is observed. The signals of the other SN2 groups of the ring appear 2.52 m.h., and 2.79 m.h., and 6.34 m.h., respectively, as above. The protons of the SN 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 6 Gts. The constant of spin-spin interactions of aromatic ring protons is JH5H7 = 7 Gts, JH7H8 = 29 Gts [1; 82-86 b, 2; 20 22 b].

Quantum chemical calculations of the formation of tertiary alcohols by the acetylthiochroman molecule on the basis of magnesium-organic compounds were also studied. Figure 3 below shows the 3D structure of 6- (1-methyl-1-oxyamyl) -1-thiochroman from data obtained using the RMZ and AM1 semi-empirical methods.

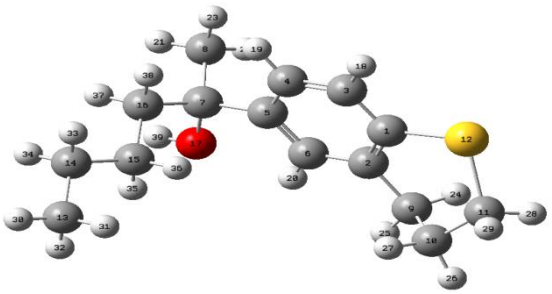


Figure 1 6- (1-methyl-1-oxyamyl) -1-thiochromanning

3D structure

According to the data obtained using the RMZ and AM1 semi-empirical methods of the 6- (1-methyl-1-oxyamyl) -1-thiochroman in Figure 2, the sulfur in this molecule has a charge value of -0.687 when the hydroxyl group belonging to the tertiary carbon atom has a charge value of -0.687. it can be seen that the charge per atom is 0.405.

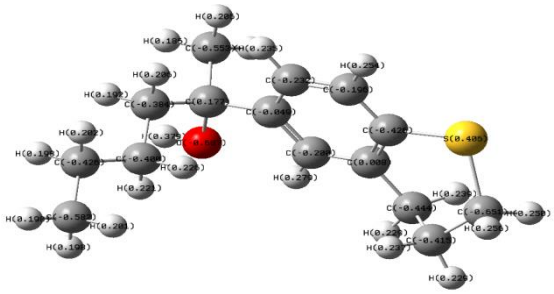


Figure 2 6- (1-methyl-1-oxyamyl) -1-thiochroman

distribution of atomic charges in the molecule

Figure 3 shows that the length of the ordinary S-S bonds in the 6- (1-methyl-1-oxyamyl) -1-thiochroman molecule is 1.54 nm and that the length of the S-N bonds is 1,122 nm. It can also be seen that the lengths of the double in the aromatic ring are 1,386 nm, respectively. With respect to the aromatic ring, it can be seen that the length of the S-O bond on the carbon atom belonging to the a-state tertiary alcohol is 1.409 nm, while the length of the O-N bond is 0.99204 nm. It can also be seen that the length of the S-S bond belonging to the heterocyclic ring in this molecule is 1.79 and the length of the S-S bond bound to the armature ring is 1.7899 nm.

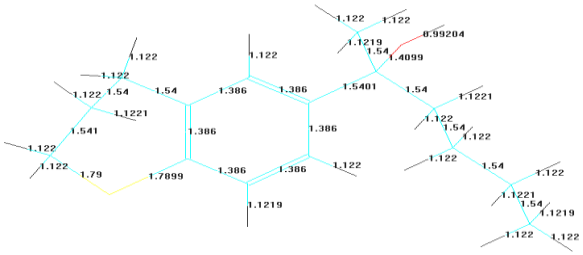


Figure 3 6- (1-methyl-1-oxyamyl) -1-thiochroman

molecule bond lengths

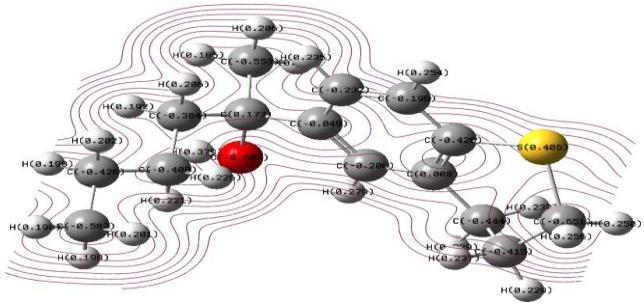


Figure 4 6- (1-methyl-1-oxyamyl) -1-thiochroman

the total electron density of the molecule

on the basis of thiochroman atsil compound synthesis of trial alcohols

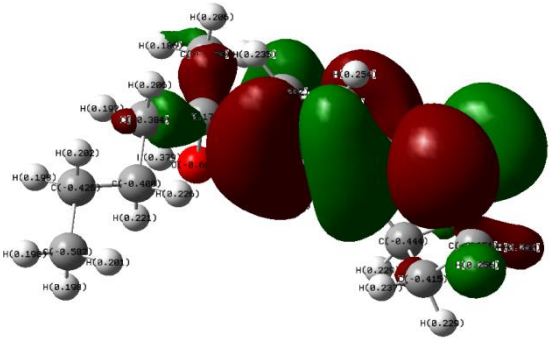


Figure 5 6- (1-methyl-1-oxyamyl) -1-thiochroman

HOMO image of the molecule

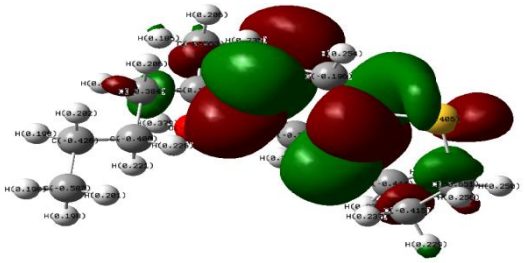


Figure 6 6- (1-methyl-1-oxyamyl) -1-thiochroman

LUMO image of the molecule

Table 3 below compares the quantum chemical characteristics of the 6-acetyl-1-thiochroman molecule obtained as the starting material with the quantum chemical characteristics of the tertiary alcohol, ie 6- (1-methyl-1-oxyamyl) -1-thiochroman molecule obtained on the basis of this molecule. options are available.

Quantum chemical calculations of compounds used

Table-3

Compounds	**Total Energias kkal/mol**	**Binding Energy kkal/мol**	**Heat of Formation, kkal/мol**	**Elektronic Energy, kkal/mol**	**Nuclear Energy, kkal/mol**
Starting substances					
6-Acetyl-1-thiochroman	-45390,0219	-2653,33058	-22,357583	-258690,595	213300,574
Synthesized substance					
6-(1-methyl-1-oxyamyl)-1-thiochroman	-63183,9301	-3899,08036	-63,527366	-434363,510	371179,579

It is possible to predict the reactivity of the reaction centers in the molecule by analyzing the electronic structure and energy properties (total energy, formation energy, heat of formation, electron energy, nuclear energy) of the substances obtained as quantum chemical characteristics of these studied substances. a number of targeted reactions can be carried out [3; 107348, 4; 100732].

CONCLUSION

The study of the reaction of tertiary alcohols on the basis of thiochroman acyl derivatives showed that the yield of the reaction product increases in parallel with the increase in the mass of the active reagent. All obtained thiochroman series tertiary alcohols are soluble in organic solvents, have a peculiar pleasant odor and bright reddish color. Thus, instead of a conclusion, it can be said that thiochroman series acyl derivatives behave in the same way as aliphatic and aromatic ketones in their reactions with magnesium compounds and form tertiary alcohols corresponding to high yields.

REFERENCES

1. Рахматова Г.Б., Курбанов М.Ж., Рузибоев М.Т.. Синтез и изучение скорости реакции ацилирования 1-тианданов и 1-тиохроманов. Universum: Химия и биология Выпуск: 12(66)Декабрь 2019 Москва 2019. 82-86 стр
2. Rakhmatova G.B., Kurbanov M. J., Turabayeva N.B. Tursunova G.K.. Study of inspactive properties against corrosion of α-aminocetones and their products// Austrian Journal of Technical and Natural Sciences. №5-6, -2020. -P.54-59.
3. Abir Saagama, Nouriddin Issaoi. Design molekulardocking analysisofan anti inflammatory dru, computational analysis and intermolecular interactions energy studies of 1-benzothiophene-2-carboxylik acid. Computational Biology and Chemistry. Volume 88, October, 2020, 107348.
4. Athishu Entoni, Nethaji P., Rajaraman D. Synthesis, spectral characterization, crustal exzamination, DFT method and molecular docking studies of 1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-(thophen-2-yl)-1H-phenanthro[9,10-d]imidazole. Chemecal Data Collections. Volume 34, August 2021, 100732.
5. Rakhmatova G.B., Kurbanov M.J., Xidirova Z.U. Studius of the anticorrozive properties of sulfur containing bicyclica aminoketones // Journal of Critical Reviews., ISSN-2394-5125. vol 7., Isue 3., 2020., 63-68. https://www.scopus.com /sourceid/21100920227