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ORGANIC CHEMISTRY

**6-ACETETHYL-1-THIOXROMANE AND 7-ACETETHYL-6-METHYL-1-THIOXROMANE
 ACETIC ETHER CONDENSATION REACTIONS WITH**

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**РЕАКЦИИ КОНДЕНСАЦИИ 6-АЦЕТИЛ-1-ТИОХРОМАНА
 И 7-АЦЕТИЛ-6-МЕТИЛ-1-ТИОХРОМАНА С ЭТИЛОВЫМ ЭФИРОМ УКСУСНОЙ КИСЛОТЫ**

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ABSTRACT

The condensation reactions of acetyl derivatives of the thiochroman series with ethyl acetic acid have been studied. As a result of the reaction, it was established that compounds of the acetylthiochroman series result in the reaction with good yield of the corresponding thiochromanoyl acetones.

АННОТАЦИЯ

Изучены реакции конденсации ацетилпроизводных ряда тиохромана с этиловым эфиром уксусной кислоты. В результате реакции установлено, что соединения ряда ацетилтиохромана в результате реакции с хорошим выходом образуются соответствующие тиохроманоилацетоны.

Keywords: thiochroman, acylthiochroman, circaethyl ether, diketone, sodium chromanoylacetone.

Ключевые слова: тиохроман, ацилтиохроман, циркуэтиловый эфир, дикетон, хроманоилацетон.

Introduction

It is known that the condensation reactions of complex esters with ketones lead to the formation of β -diketones. Most ketones can easily undergo enol tautomerization in the presence of bases or acids if they have hydrogen atoms on the α -carbon atom relative to the keto group. For diketones and ketones, the amount of enols at equilibrium is stabilized by the additional unsaturation groups in their enol form. The amount of enols formed from ketones depends strongly on the structure of the ketone and the nature of the solvent used. [1; 82-86 p].

Materials and methods

Synthesis of 6-thiochromanoylacetone (I)

For the synthesis of 6-thiochromanoylacetone molecule, we equipped a 50 ml round-bottomed, two-necked flask with a refrigerator and a bifurcated flask with the upper part of the refrigerator fixed with a tube of dehydrated calcium chloride, and added 1.92 g (0.01 mol) of 6-acetyl-1-thiochroman and Add 20 ml of dry circaethyl ether and 10 ml of absolute ether. After that, we slowly add 0.2 g of sodium metal cut thinly from the

second neck of the flask and keep the reaction mixture in a boiling water bath for 45 minutes. Then let the reaction mixture in the flask cool to room temperature. We filter the resulting sodium chromanoyl acetone. Then we wash the resulting sodium chromanoyl acetone with a small amount of circethyl ether. Then squeeze it dry between two filter papers. Put the obtained product in a glass, dissolve it in a small amount of water and pass it through a filter. Cool the filtrate with ice and acidify in a 50% acetic acid solution to an acidic medium. The precipitate falls. The formed crystals are filtered, washed in cold water and dried in a desiccator. The yield of the product, 6-thiochromanoylacetone, is 1.5 g or 64%. Liquefaction temperature is 41-42 °C. Elemental analyses, found, % : S 71.80; N 6.54. Calculated for the formula $C_{13}H_{14}O_2S$, %: S 71.61; N 6.46.

Synthesis of 6-methyl-7-thiochromanoylacetone (II)

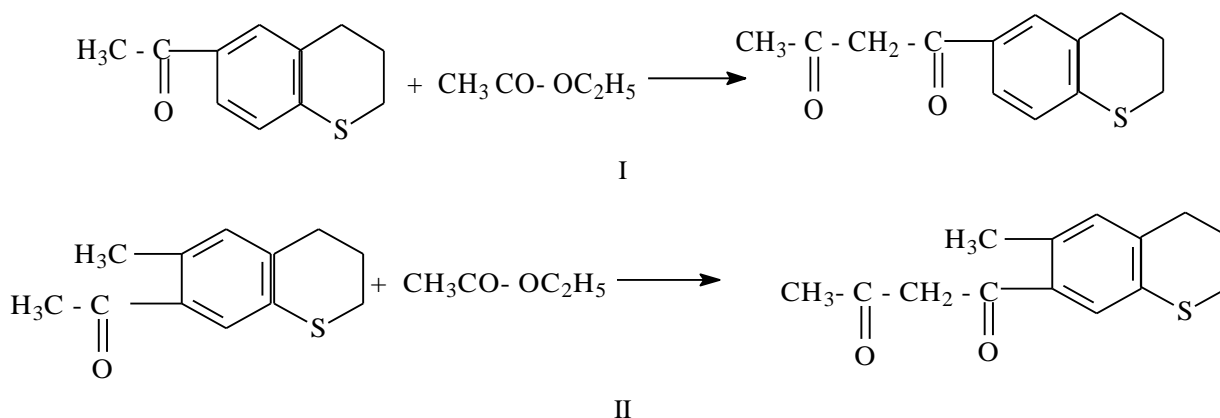
The synthesis of this substance was carried out in the same way as the synthesis of substance 1 above. A solution of 2.2 g (0.096 mol) of 6-methyl-7-acetyl-1-thiochromene and 20 ml of dry circethyl ether in 10 ml of absolute ether was taken for the reaction. The yield of

the product, 6-methyl-7-thiochromanoylacetone, was 1.4 g or 56%. Liquefaction temperature 38-39 °C. Elemental analysis, found, % : S 67.91; N 6.58. Calculated for the formula C₁₄H₁₆O₂S, %: S 67.76; N 6.45.

Results

To synthesize β-diketones of the acetylthiochroman series, we conducted condensation reactions of complex esters. Condensation reactions of 6-acetyl-1-thiochroman and 7-acetyl-6-methyl-1-thiochroman molecules with circaethyl ether were studied for the reaction. The reaction was carried out for 40-45 minutes in the presence of metallic sodium in an absolute ether environment in equimolecular proportions of reacting reagents.

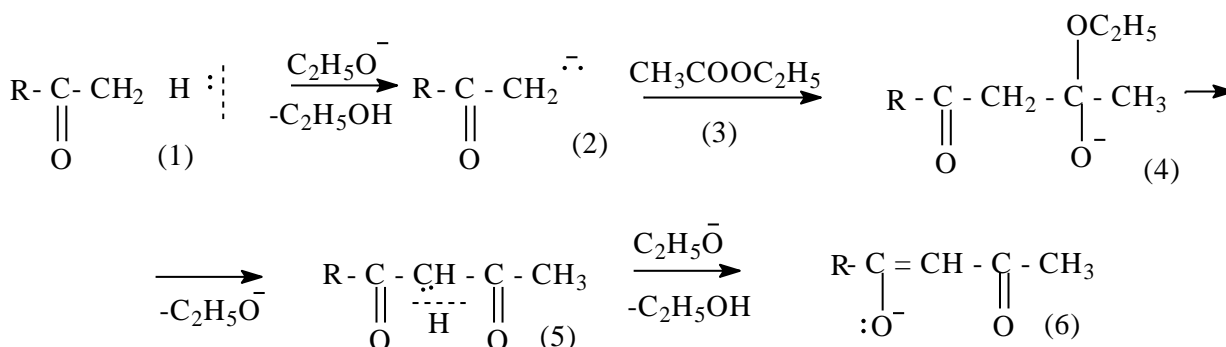
The reaction takes place with acetylthiochroman derivatives in the presence of sodium metal in the form of dry circaethyl ether in an absolute ether environment. First, the reaction mixture was left in a boiling water bath for 45 min and then allowed to cool to room temperature. The resulting sodium chromanoylacetone was dissolved in a little water, acidified in a 50% acetic acid solution to an acidic medium, and collected as a precipitate. The yield of the product, i.e. 1-thiochromanoylacetone (I) is 64%. By treating the last products, i.e. sodium chromanoylacetones with 50% acetic acid solution, the corresponding β-diketones with a symmetrical structure were obtained:



As it can be seen from the above reaction scheme, 6-methyl-7-thiochromanoylacetones (II) were synthesized in 56% in the same reaction under the same conditions. As it can be seen from the yields of the reaction products, it was found that in the reaction of the above compounds with circaethyl ether, the productivity of the monosubstituted derivatives is slightly higher than that of the disubstituted derivatives of the aromatic ring. This indicates that the acetyl group on the aromatic ring reduces the electron density of the aromatic ring, which in turn facilitates the attack of nucleophilic reagents on the aromatic ring. However, although the above compound

II has an electron acceptor group that increases the attack of nucleophilic reagents on the aromatic ring, the adjacent methyl group increases the internal electron density of the aromatic ring due to its positive inductive effect. It can be seen that the presence of both electron-donating and electron-accepting groups in the aromatic ring of one molecule affects the yield of the product in any reaction.

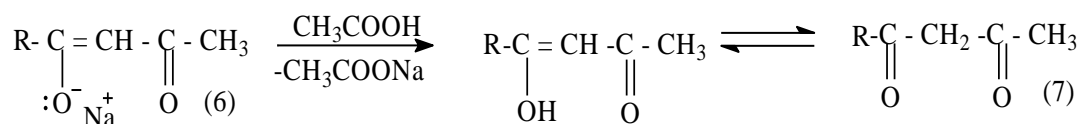
The resulting compounds are crystalline substances, soluble in organic solvents, but insoluble in water. The mechanism of the condensation reaction of ketones of the acetylthiochroman type with circaethyl ether can be expressed in the following order:



R= thiochromene molecule.

The catalyst (ethylate anion) removes a proton from ketone (1), which is a methylene component. The resulting highly reactive carbanion (2) attacks the partially positively charged carbon atom of ethyl ether (3) of acetic acid, which is a carbonyl component. As a result,

anion (4) is formed, and thiochromanoylacetone (5) is obtained due to the separation of the ethylate ion. This compound exists as the enolate form (6) in alkaline media. The reaction mixture is acidified to isolate thiochromanoylacetones:



The structure of the synthesized compounds was determined using IR- and PMR-spectra, and the composition was determined using the method of elemental combustion analysis. Monitoring the progress of the reaction and determining the purity of the obtained substances was carried out using the thin-layer chromatographic method on the 'Silufol' plate [2; pp. 7322-7328, 3; pp. 5229-5233, 4; 8160-8169 b].

In the PMR-spectrum of 2-methyl-1-thiaindanoylacetone (I), protons of the methyl group in the sixth position appear as a singlet at 1.27 m.u. show their signals in the signals of methylene group protons are 2.13 m.u. in the form of a complex multiplet and 2.32 m.u. gives its signals, while the signals of protons in the aromatic ring are 8.28 m.u. and 8.32 m.u. appears. The characteristic aspect of the spectrum of this substance lies in the presence of a strong internal molecular hydrogen bond in compounds with this structure. As the acidity of β -diketones in the form of enol increases, the shift of the signals of the hydroxyl group indicates that the dark area shifts to the side. A similar appearance is shown by the enol-form molecule of 1-thiochroman β -diketones in the complex multiplet form of the proton

in the hydroxyl group at 2.08 m.u. manifestation and the signals of the proton in the SN group of α -carbon atom are 7.12 m.u. can be seen in their manifestations.

In the IR-spectrum of the synthesized thiochromane series β -diketones, broad absorption lines of the OH group in the form of enol can be seen in the region of 3570-3420 cm^{-1} . Also, the absorption lines belonging to the broad carbonyl group can be observed in the region of 1600 cm^{-1} , and the absorption lines in the region of 1310-1360 cm^{-1} indicate that they belong to CH_3CO . It shows the characteristic absorption lines belonging to the methylene group at 1445 cm^{-1} , and the absorption lines at 1100, 1065 and 1010 cm^{-1} belong to the $\text{C}=\text{C}$ double bond in the enol form. Absorption lines of characteristic vibrations of CH bonds in the benzene ring are observed in the region of 840 cm^{-1} , while absorption lines corresponding to valence vibrations of hydrogen atoms in the benzene ring can be observed in the region of 930 and 950 cm^{-1} . From the obtained results, it can be said that in these compounds, the lifetime of the structure in the enol form is much better than in the keto form.

The table below presents the physicochemical data of the β -diketones of the thiochromane series.

Table 1.

Thiochromane series β -diketones physical and chemical data

O/N	Percent, %	Liquidus temperature °C.	Found, %		Gross formula	Calculated, %	
			C	H		C	H
I	64	41-42	71,85 71,80	6,59 6,54	$\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}$	71,61	6,46
II	56	38-39	67,91 67,87	6,58 6,55	$\text{C}_{14}\text{H}_{16}\text{O}_2\text{S}$	67,76	6,45

Conclusion

As it can be seen from the above information, it was found that in the reaction of 6-acetyl-1-thiochroman and 6-methyl-7-acetylthiochroman molecules with circaethyl ether, the reactivity of 6-acetyl-1-thiochroman molecule is slightly higher than that of 6-methyl-7-acetylthiochroman molecule. The main reason for this can be attributed

to two factors. The first factor is the steric effect of the methyl group in the 6-position. The second factor can be explained by the influence of electron-donor and electron-acceptor groups in the aromatic ring. Thus, it turned out that semi-aromatic sulfur-containing bicyclic compounds, like aliphatic and aromatic ketones, are well suited to complex ether condensation reactions.

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