

SYCAETYL ETERY OF 6-ACYTYL-1-THIOCHROMAN AND 7-ACYTYL-6-METHYL-1-THIOCHROMAN CONDENSATION REACTIONS WITH

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Abstract. Condensation reactions of acetyl derivatives of thiochromane series with acetyl ether were studied. As a result of the reaction, it was found that acetylthiochromane compounds react with acetyl ether in the same way as aliphatic and aromatic ketones, and the reaction produces thiochromanoilacetones with good yields.

Keywords: thiochroman, acylthiochroman, acetyl ether, diketone, sodium thiohrmanolate acetone, filtrate, desiccator, electron donor, electron acceptor, carbonyl group, ketone, absolute ether, charge, reagent.

INTRODUCTION

It is known that the condensation reactions of esters with ketones lead to the formation of--diketones. In most ketones, if there are hydrogen atoms in the α -carbon atom relative to the ketogen group, they can easily undergo enol tautomerization in the presence of bases or acids. For diketones and ketones, the equilibrium amount of enols in them is stabilized by the addition of unsaturated groups in the form of an enol. The amount of enols formed from ketones is strongly dependent on the ketone structure and the nature of the solvent used [1; 82-86 p].

MATERIALS AND METODS

Synthesis of 6-thiochromanoilacetone (I)

To synthesize the 6-thiochromanoilacetone molecule, we equip a round-bottomed 50 ml volumetric flask with a two-horn forshtos attached to the refrigerator and the top of the refrigerator with a dehydrated calcium chloride tube and add 1.92 g (0.01 mol) of 6-acetyl-1-thiochroman. Add 20 ml of dry vinegar and 10 ml of absolute ether. Then slowly add 0.2 g of metallic sodium, finely chopped from the second throat of the forshtos, and keep the reaction mixture in a boiling water bath for 45 minutes. The reaction mixture in the flask is then allowed to cool to room temperature. We filter the

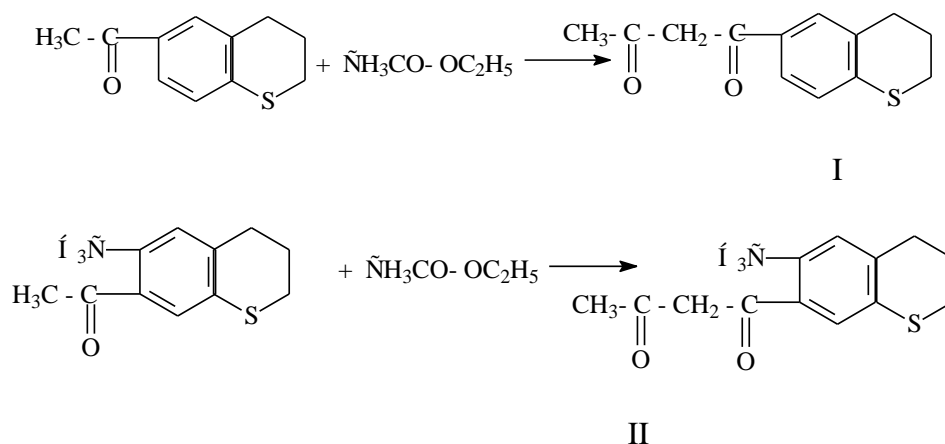
resulting sodium thiochromanolate acetone. We then wash the sodium thiochromanoilacetone formed with a small amount of acetyl ether. then squeeze it between two filter papers and let it dry. Put the resulting product in a glass, dissolve it in a little water and filter. Cool the filtrate with ice and acidify it in a 50% acetic acid solution to an acidic medium. The sink falls. The resulting crystals are filtered, washed in cold water and dried in a desiccator. The yield of the product, ie 6-thiochromanoilacetone, is 1.5 g or 64%. Liquidus temperature 41-42 °S. Element analysis, found,%: C 71,80; H 6,54. C₁₃H₁₄O₂S %: Calculated for formula, C 71,61; H 6,46.

Synthesis of 6-methyl-7-thiochromanoilacetone (XII)

The synthesis of this substance was carried out in the same way as the method of synthesis of the 1 substance above. For the reaction, 2.2 g (0.096 mol) of 6-methyl-7-acetyl-1-thiochroman and 20 ml of dry acetate ether solution in 10 ml of absolute ether were obtained. The yield of the product, ie 6-methyl-7-thiochromanoilacetone, is 1.4 g or 56%. Liquidus temperature 38-39 °S. Element analysis, found,%: C 67,91; H 6,58. C₁₄H₁₆O₂S Calculated for formula, %: C 67,76; H 6,45.

REZULTS (DISCUSSION)

To synthesize the - diketones of the acetylthiochromane series, we conducted condensation reactions of the esters. Condensation reactions of 6-acetyl-1-thiochromane and 7-acetyl-6-methyl-1-thiochromane molecules with acetyl ether were studied for the reaction. The reaction was carried out in the equimolecular ratios of the reactants in an absolute ether medium in the presence of metallic sodium for 40-45 minutes. The reaction with acetylthiochroman derivatives requires the presence of dry acetyl ether in the presence of metallic sodium in an absolute ether medium. The reaction mixture is first left in a boiling water bath for 45 minutes and then cooled to room temperature. The resulting sodium thiochromanoilacetone was dissolved in a small amount of water, acidified in a 50% acetic acid solution to an acidic medium, and precipitated. The yield of the product, i.e. 1-thiochromanoilacetone (I), is 64%. Appropriate b-diketones with a symmetrical structure were obtained by processing the final products, ie sodium thiochromanolate acetones, with a 50% acetic acid solution:

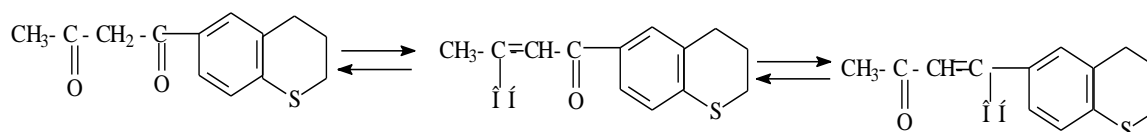


As can be seen from the above reaction diagram, 6% of 6-methyl-7-thiochromanoilacetones (II) were synthesized under the same conditions in the same reaction. It can be seen from the products of the reaction products that in the reaction of the above compounds with acetyl ether it was found that

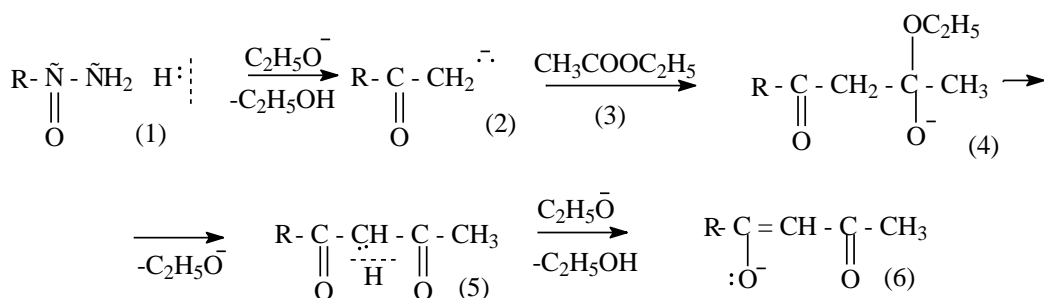
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the yield of the product was slightly higher in mono-exchange products than in the dialmashing products in the aromatic ring. This indicates that the acetyl group in the aromatic ring reduces the electron density of the aromatic ring, which in turn facilitates the attack of nucleophilic reagents on the aromatic ring. However, while the above compound is an electroacceptor group in substance II that enhances the attack of nucleophilic reagents in 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 an electron donor group and an electron acceptor group in the aromatic ring of a single molecule has an effect on the output of the product in any reaction.

The appearance of b-diketones in the enol form was found to be higher in solution than in the keto form. A similar pattern is observed in 1-thiochromane series b-diketones.

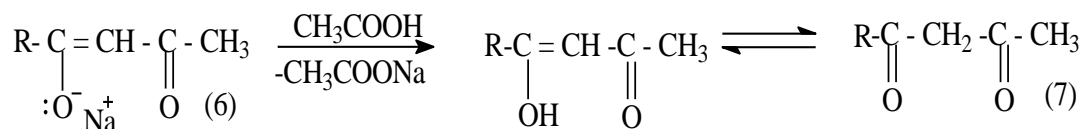


The resulting compounds are crystalline substances, soluble in organic solvents and insoluble in water. The mechanism of the reaction of condensation of ketones of the acetylthiochromane type with acetyl ether can be expressed in the following order:



where: R = thiochroman molecule.

The catalyst (ethylate-anion) transfers a proton from the ketone (1), which is a methylene component. The resulting reactive ability attacks the partially positively charged carbon atom of ethyl ether (3) of acetic acid, which is a carbonyl component of high carbonion (2). As a result, an anion (4) is formed, from which thiochromanoilacetone (5) is obtained due to the separation of the ethylate ion. This compound is in the form of an enolate form (6) in an alkaline environment. The reaction mixture is acidified to separate thiochromanoilacetones:



The structure of the synthesized compounds was determined using IR- and PMR-spectra, and the composition was determined by the method of analysis by burning the elements. Control of the reaction and determination of the purity of the obtained substances was carried out on a plate "Silufol" using a thin-layer chromatographic method [2; 7322-7328 b., 3; 5229-5233 b., 4; 8160-8169 b].

In the PMR spectrum of 2-Methyl-1-thiaindanoilacetone (I), the protons of the methyl group in the sixth state are singlet-shaped at 1.27 m.u. The signals of the protons of the methylene group are in the form of a complex multiplet of 2.13 m.u. and 2.32 m.u. while the signals of the protons in the aromatic ring are 8.28 m.u. and 8.32 m.u. appears. A characteristic feature of the spectrum of this substance is the presence of a strong internal molecular hydrogen bond in the compounds having this structure. As the acidity of α -diketones in the enol form increases, the shift of the hydroxyl group signals indicates a shift in the direction of the sheep field. A similar appearance is observed in the enol-shaped molecule of 1-thiochroman--diketones in the form of a complex multiplet of a proton in the hydroxyl group at 2.08 m.u. and the signals of the proton in the SN group on the α -carbon atom are 7.12 m.u. can be seen when they appear.

In the IR spectrum of the synthesized thiochromane series β -diketones can be seen broad absorption lines of the ON group in the form of enol in the area of 3570-3420 cm^{-1} . It is also possible to observe the absorption lines belonging to the broad-spectrum carbonyl group in the area of 1600 cm^{-1} , while the absorption lines in the area of 1310-1360 cm^{-1} indicate that they belong to SN3SO. The characteristic absorption lines belonging to the methylene group show that the absorption lines in the 1445 cm^{-1} area and the absorption lines in the 1100, 1065 and 1010 cm^{-1} areas belong to the enol form S = S pair. The characteristic oscillations of the SN bonds in the benzene ring can be observed in the absorption lines 840 cm^{-1} , while the absorption lines corresponding to the valence oscillations of the hydrogen atoms in the benzene ring can be observed in the 930 and 950 cm^{-1} regions. From the results obtained, it can be concluded that the lifetime of the enol form is much longer than the keto form in these compounds.

The following table shows the physicochemical data of thiochromane series β -diketones.

Of th-chroman series β -diketones

physicochemical

Table-1

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

CONCLUSION

From the above data, it was found that the reaction capacity of the 6-acetyl-1-thiochroman molecule and the 6-methyl-7-acetylthiochroman molecule with acetyl ether was slightly higher than that of the 6-acetyl-1-thiochroman molecule. The main reason for this can be attributed to two factors. The first factor is that a slight decrease in the reaction yield in this 6-methyl-7-acetylthiochroman molecule

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can be explained by the steric effect of the methyl group in the 6-state. The second factor can be explained by the effect of the electron donor and electron acceptor groups in the dialmashed aromatic ring. Thus, it was found that bicyclic compounds containing sulfur-containing sulfur, like aliphatic and aromatic ketones, are well involved in complex ether condensation reactions.

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