Catalytic Acylation Of 3-Benzylbenzoxazoline-2-On With Aliphatic Acid Chlorangrid

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Abstract: In this article the acylation 3-benzylbenzoxazolinon-2-ones which are hetero combinations with an aliphatic acid the result of acylation are given with the presence of small amounts of $FeCl_3 6H_2O$. It is found out that the agent not going to the benzyl group which in 3-benzylbenzoxazolinon-2-ones but going to the condition benzoxazolinon-2-ones` molecule. In this reaction, 3-benzyl-6-acilbenzoxazol-2-ones` synthesis is carried out for the first time. Besides in the chloroacylation reaction of 3-benzyl-6-acylbenzoxazolinon-2-ones it is found the relative activity row of different kinds of catalyst.

Index Terms: acylating, aliphatic acid chlorides, benzaxozolin-2-on, 3-benzylbenzoxazolin-2-on, 3-benzyl-6-acylbenzoxazolin-2-ones, catalizatory, lewis acid.

1. INTRODUCTION

Currently, most of the drugs used in various sectors of the economy are organic and the demand for them is increasing day by day. Therefore, one of the most important tasks of chemistry is to develop effective methods for obtaining organic compounds and finding their economically viable sources. In this regard, the aromatic and heterocyclic compounds have the potential to be used by the acylating reactions of Friedel-Krafts reaction. Until now, these reactions have been extensively studied in the example of aromatic compounds, but the five-membered heterocyclic compounds condensed by aromatic rings have not been well studied in the example of benzazoline-2-ones. Benzazolin-2-one like derivatives are practically essential compounds. Among the compounds of this class, substances with a broad biological spectrum (herbicides, fungicides, bactericides and other drugs) have been used in various fields of the national economy. Due to the natural biological activity of benzoxazoline-2-on and its methoxy derivatives, the resistance of some plants to fungal diseases increases. Benzoxazolin-2-on is extracted from barley content, 6-methoxy- and 6,7-dimethoxybenzoxazolin-2-on from the roots of the Coix Lacryma Jobi and Scoporia dulcus plants [1-3]. At the same time, benzazoline-2-ones are also chemically important. There are several reaction centers in their molecules: carbonyl group in the second state, heteroatoms (nitrogen and oxygen) in the first and third states, and two aromatic rings. Therefore, substances of this class may react in different directions with electrophilic reagents.

2. DISCUSSION

In recent years, we have been developing methods for the acylatic synthesis of aromatic and heterocyclic compounds with a small number of catalysts that are economically feasible and relevant. Analysis from the literature reveals that Lewis acids with strong (AlCl3) and moderate strength (FeCl3, ZnCl2, SnCl4, etc.) have the best activity as catalyst in acetylation reactions. They form a strong donor-acceptor bond with acetylation agents. As the bond strength increases, the polarity of the carbonyl group to the adsorption agent increases, which in turn increases the positive charge of carbonyl carbon. This facilitates the electrophilic attack of the aromatic and heterocyclic compounds by the absorbing agent [4,5]. In the Friedel-Krafts reaction, the equimolar or excess catalysts activate the acid chlorangrid and determine the course of the process. However, when the catalyst is used in small quantities, the presence of Lewis acids is not only limited to the activation of chlorangids, but also to the formation of a solid complex with reaction products. In the first step, the catalyst forms a complex A with an acylating agent:

$$RCOCl + MXn \rightleftharpoons \underset{A}{RCOCl \cdot MXn}$$

The rate of formation of this complex depends on the activity of the catalyst, the stronger its receptor properties, the easier it is to interact with chlorangride. During the second phase of the reaction, this complex forms a complex (B) of the reaction product with the catalyst as a result of an attack on the aromatic ring:

$$ArH + \underset{A}{RCOCl \cdot MXn} \rightarrow \underset{B}{ArCOR \cdot MXn} + HCl$$

The formation of this complex has a slowing effect on the acceleration process. The complexes of the reaction products formed by the strong Lewis acids do not break down, which leads to a slowdown in the process. The complexes of the reaction products formed by weaker Lewis acids are easily dispersed, which allows the process of acetylation. However, it should also be borne in mind that the free chlorangrid in the reaction mixture also contributes to the decay of complex B:

$$\underset{B}{ArCOR \cdot MXn} + RCOCl \rightarrow ArCOR + \underset{A}{RCOCl \cdot MXn}$$

Usually, acylating reactions with low levels of Lewis acids react at higher temperatures. This also leads to the breakdown of complex B and the released catalyst continues to function. Due to the factors listed above, it is possible to disperse aromatic and heterocyclic compounds in the presence of a small amount of catalysts.

As mentioned above, when used in small quantities in catalyst reactions, their activity differs from that used in equimolar quantities. The strongest Lewis acids (AlCl3) are not active in acetylation reactions as they form a solid complex with reaction products. Consequently, the weaker Lewis acids, which form sufficiently active (A) and acetylene (B) complexes with reaction agents, should have higher activity in these reactions. This has been proven in some studies [6-9], with the highest activity of the relatively weak Lewis acids - FeCl3 and FeCl3·6H2O. In order to study the electrophilic exchange

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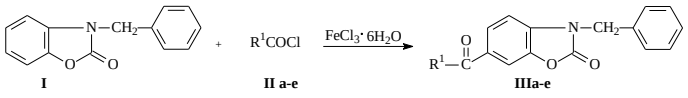
reactions of benzoxazolin-2-ones, we aimed to study the reaction of 3-benzylbenzoxazolin-2-ons with the addition of aromatic ring to its molecule. While the presence of two aromatic rings in these molecules makes them chemically important, the fact that their biological activity data are not recorded in the literature is practical. Of particular interest was the study of the reaction of 3-benzylbenzoxazolin-2-ons with aliphatic acid chlorangridides in the presence of a small amount of catalysts. 3-Benzylbenzoxazolin-2-on (I) aliphatic acid chloranghydrides IIa-e (хлорсирка, н-мой, изомой, н-валериан ва изовалериан кислота хлорангидриди) in the presence of FeCl3·6H2O (reagents mol. I:IIa-e:FeCl3.6H2O = 1:1,5:1.10-2) The reaction of 150–1600C under solvent conditions was investigated and the reaction products were obtained from 3-benzyl-6-acylbenzoxazolin-2-them (IIIa-e) (Table 1).



II, III a R^1=$ClCH_2$; **II, III b** R^1=n-C_3H_7; **II, III c** R^1=i-C_3H_7; **II, III d** R^1=n-C_4H_9; **II, III e** R^1=i-C_4H_9;

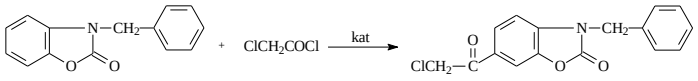
3 RESULTS

The structure of the synthesized 3-benzyl-6-acylbenzoxazoline-2-ions (IIIa-e) was confirmed by IR, NMR 1H spectroscopy, mass spectrometry and element analysis. Observation of the absorption curves in their IR spectra of the 6-position carbonyl group valence oscillations (1660-1680 cm-1) and the unstable deformation oscillations of the CN fragment of the 1,2,4-volatile ring (805-825 and 870-885 sm-1). is possible. The presence of molecular ions and fragments confirming the proposed structure in the mass spectra of matter was determined. The structure of the synthesized 3-benzyl-6-acylbenzoxazoline-2-ions (IIIa-e) is also confirmed by their NMR 1H-spectra. In the aromatic section of benzoxazolin-2-on, the duallet of 4-position hydrogen J=8.35 Hz (7.04-7.23 mA), J=8.40, and J=1.68 Hz ortho dual couplings of hydrogen 5-state meta-constants (7.65-7.77m.u) and duplexes of 7-state proton-state meta-constants J=1.68 Hz (7,80-7,94 mu). It happened. The protons in the aromatic ring of the benzyl group are 7.05-7.25 m.p. in the field, and protons of the methylene group are 4.85-4.88 m.p. appeared in the field as a multiplet. The protons of the acyl residue formed a chemical shift in a relatively strong area (0.85-3.58 mU). Of particular interest was the study of the relative activity of catalysts used in acetylation reactions involving 3-benzylbenzoxazoline-2-ions with a small amount of catalysts. Therefore we have investigated 3-benzylbenzoxazoline-2-on (I) chloracetylchloride FeCl3, FeCl3. 6H2O, FeCl3.12H2O, ZnCl2, ZnCl2.2H2O, AlCl3 and iron acetylacetonate (TAA) were studied (ratio of reagents I:IIa:catalyst = 1:1,5:1.10-2). The reactions were carried out by heating at 150–160°C for 3 h, and synthesis of 3-benzyl-6-chloracetylbenzoxazoline-2-on was performed in all cases. These reactions revealed the relative activity of different catalysts under the same conditions. In addition, the structure of 3-benzyl-6-chloracetylbenzoxazoline-2-on (IIIa) was also confirmed by indirect synthesis. The results of the work is given on Table 2.

TABLE 1

Productivity of 3-benzyl-6-acylbenzoxazolin-2-ons (IIIa-e), fluid temperature, results of element analysis and spectral characteristics

Attachment	Brutto formula	T.l., ^{0}C (solvent for recrystallization)	Productivity,%	Found, N% Defined, N%	Mass spectrum M$^+$ (m/z)	IR spectrum, γ, cm^{-1} C=O 6-case	C=O 2- case
III a	$C_{16}H_{12}NO_3Cl$	162-164 (ethanol)	51	4.55 4.64	301/303	1660	1780
III b	$C_{18}H_{17}NO_3$	160-162 (ethanol)	58	4.68 4.74	295	1660	1780
III c	$C_{18}H_{17}NO_3$	153-155 (benzene)	67	4.63 4.74	295	1675	1787
III d	$C_{19}H_{19}NO_3$	145-147 (hexane)	72	4.47 4.53	309	1660	1770
III e	$C_{19}H_{19}NO_3$	133-135 (ethanol)	79	4.45 4.53	309	1670	1770



catalizator = FeCl3, FeCl3. 6H2O, FeCl3.12H2O, ZnCl2, ZnCl2.2H2O, AlCl3, TAA

TABLE 2

The results of chloracetylation of 3-Benzylbenzoxazoline-2-on with the presence of a small amount of different catalysts

The catalyst	The yield of 3-benzyl-6-chloracetylbenzoxazoline-2-on (IIIa) over time,%					
	0,5 hours	1 hours	1,5 hours	2 hours	2,5 hours	3 hours
$FeCl_3$	21	28	36	41	47	49
$FeCl_3·6H_2O$	23	29	37	42	49	51
$FeCl_3·12H_2O$	22	29	34	40	45	48
$ZnCl_2$	12	18	22	25	33	39
$ZnCl_2·2H_2O$	13	19	25	27	34	41
$AlCl_3$	Very few	Very few	3	5	6	8
TAA	5	7	9	12	18	33

6 CONCLUSION

It has been shown that the acylated products of benzyl chloride 6-chlorine-acetylbenzoxazolin-2-on, which are known to be in the same phase, are identical to those of 3-benzyl benzenzoxazoline-2-on. Their IR spectra are the same, the fluid temperature of the compounds does not cause depression. It shows that FeCl3. 6H2O, AlCl3, and TAA exhibited the highest activity in the chloracetylation of 3-benzyl benzenzoxazoline-2-on (I). In the initial phase of the chloracetylation reaction, the rate of complex formation with chloracetylchloride is higher in FeCl3 than in ZnCl2, which can be explained by the high acidity of FeCl3. The lower activity of ZnCl2 in the initial phase of chloracetylation can be explained by its low ability to form complex and its electrophilicity of the resulting complex. The low activity of TAA in the initial phase can be explained by the induction period required for its conversion to the appropriate chloride. The lowest product of the reaction product in the case of AlCl3 is the result of its formation of a solid complex with an acyl product. Based on the foregoing, the following lines of relative activity of the catalyst were found: FeCl3. 6H2O> FeCl3> FeCl3. 12H2O> ZnCl2.2H2O> ZnCl2> TAA> AlCl3 The range of activity found is consistent with the relative activity sequence found in the accumulation of various aromatic and heterocyclic compounds [9,10]. Thus, the reactions of 3-benzyl benzenzoxazoline-2-on with aliphatic acid chlorangrid were studied and synthesis of 3-benzyl-6-acylbenzoxazolin-2-them (IIIa-e) with high yield was performed. It was found that the acetylating agent moves to the 6th state in the benzoxazoline-2-on molecule, rather than

the benzyl group in the molecule of 3-benzyl benzenzoxazoline-2-on. PART OF THE EXPERIENCE Reactions and purity of the substances were monitored by thin-layer chromatography. (Silufol UV-254 System benzene-ethanol 5: 1, 1g KMnO4 + 4ml H2SO4 + 96 ml H2O or iodine vapor). Synthesis of 3-Benzyl-6-Chloracetylbenzoxazoline-2-on (IIIa) The tubes were filled with 2.25 g (10 mmol) 3-benzyl benzenzoxazolin-2-on (I) into the tubular tubular 1.69 g (15 mmol) chloracetylchloride (IIa) and 0.027 g (0.1mmol) catalyst FeCl3 • 6H2O. The reaction mixture was stirred in the oil bath at 140-1500C for 4 h. The reaction mixture was cooled to room temperature and treated with water and the precipitate filtered and crystallized in alcohol. The other 3-benzyl-6-atylbenzoxazolin-2-ones (IIIb-e) presented in the table were obtained by the above method. Indirect synthesis. Synthesis of 3-Benzyl-6-Chloracetylbenzoxazoline-2-on (IIIa) 2.115 g (10 mmol) 6-chloratsetylbenzoxazoline-2-on, 4 g (100 mmol) NaOH, 40 ml water, 40 ml benzole and 1.29 g (4 mmol) at 1,888 g (15 mmol) at 200C benzylchloride is added. The reaction mixture was kept at this temperature for 6 hours by increasing the temperature to 600C. The organic layer is separated, washed with water, and the solvent is pumped out, recrystallized from ethanol. 2.26 g (75%) of compound IIIa was obtained.

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