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NATURAL SCIENCES

CATALYTIC ACYLATION OF 6-BROMOBENZOXAZOLIN-2-ONE WITH AROMATIC ACID CHLORIDE ANHYDRIDES

Takhirov Yuldash Rajabovich
Associate professor, Urgench State University named after Abu Rayhan Beruni,
Department of Chemistry, Urgench, Republic of Uzbekistan
Ashirov Mansur Allanazarovich
PhD in Chemistry, Senior Scientific Researcher at the Khorezm Ma’mun Academy,
Urgench, Republic of Uzbekistan

Abstract This paper presents the results of the acylation reaction of 6-brombenzoxazolin-2-on with aromatic acid chlorangrides in the presence of low-grade catalyst $FeCl_3 \cdot 6H_2O$. A series of relative activities of Lewis acids as catalysts in the benzoylation of 6-bromobenzoxazolin-2-one was found.

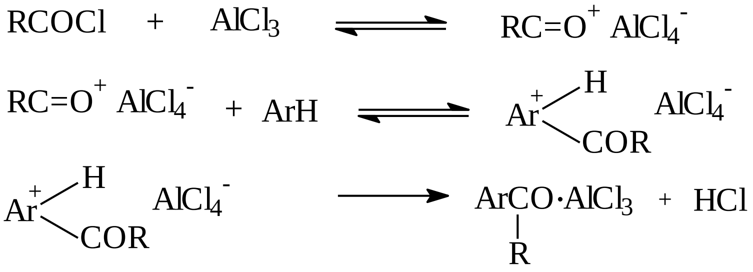
Keywords: Benzoxazolin-2-one, 6-brombenzoxazoline-2-one, catalysts, Lewis acid, acylation, aromatic acid chlorides, 3-aroyl-6-bromobenzoxazolin-2-one.

INTRODUCTION

Currently, most of the drugs used in various sectors of the economy are organic matter 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 to find their economically viable sources.

In recent years, there have been developed methods of aromatic, heterocyclic, aromatic ring condensation of heterocyclic compounds with a small number of catalysts that are economically feasible and relevant. To date, these reactions have been extensively studied in the example of aromatic compounds, but five-membered heterocyclic compounds condensed by aromatic rings have not been studied in the example of benzazolin-2-ones.

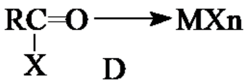
It is well known that the Friedel-Krafts reactions are electrophilic reactions in the aromatic core. At the reaction of aromatic compounds, the catalysts are subjected to polarization of acetylating agents and a carboxylic or positively charged ion pair is formed by the carbonyl group. This positively charged ion or dipole invades the aromatic ring with an electrophilic exchange reaction that occurs first through the formation of π - and then σ-complexes [1].



Generally, a good catalytic effect is observed in strong Lewis acids, which often form ionic salts (C), with weaker acids, and weaker - donor-acceptor complexes (D).

$$RCO^{+}MX^{-}_{n+1}$$

C



$$\underset{X}{RC}=O \longrightarrow MXn$$

D

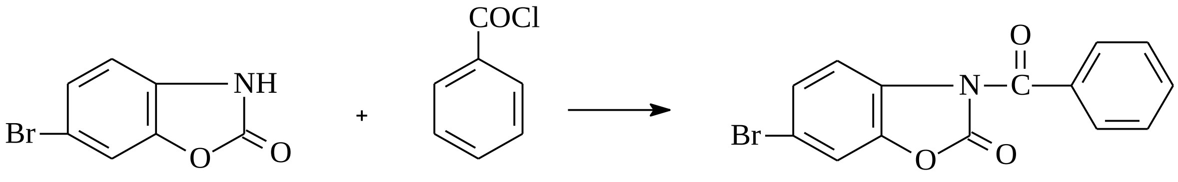
It is known that how greater the strength of Lewis acid, the donor-acceptor bond is stronger with the acne agent. The stronger the donor-acceptor bond, the higher the polarity of the carbonyl group, and the more the carbonyl group increases the positive charge of the carbon atom. This facilitates nucleophilic attack by the aromatic ring [2]. However, as stated in the literature, the role of catalysts in catalytic oxidation reactions is more complex, and it not only activates the acetylating agent but also catalyzes the reaction product and slows down the reaction. Such complexes formed by strong Lewis acids are strong, and weak complexes are easily broken down. High temperatures also cause these complexes to decompose and secrete the catalyst for further reaction [3 - 9].

As is known from the literature [10], the synthesis of benzoxazoline-2-ones by 6-acyl benzoxazolin-2-them by carbonic acid chloride hydrogen atoms in triplicate aluminum chloride. It has been reported later that these adsorption reactions can be accomplished with aromatic acid chloride hydrides in the presence of low zinc chloride [11].

RESULTS AND DISCUSSION

In order to study the feasibility of catalytic acylation reactions of 6-bromobenzoxazolin-2-one with aromatic acid chlorides, we carried out benzoylation reactions in the presence of various catalysts.

As a result of benzoylation of 6-brombenzoxazolin-2-on (**I**) with benzoyl chloride for 3 hours at $200\text{-}210^{0}C$ nitrobenzene solvent in the presence of $1.25\cdot10^{-2}$ mol $ZnCl_2$, $FeCl_3\cdot6H_2O$, iron acetylacetonate (IAA) 3-benzoil-6-brombenzoxazoline-2-on (**III**) synthesis was performed (Table 1).



I **II** **III**

In order to compare the synthesis results, the equimolar quantities of $AlCl_3$ were also studied and the expected result was not achieved. However, with increasing $AlCl_3$ up to 3 mol, the yield of 3-benzoyl-6-brombenzoxazoline-2-on (**III**) was up to 12% (Table 1).

Table 1. Benzoylation 6-brombenzoxazoline-2-on with various catalysts

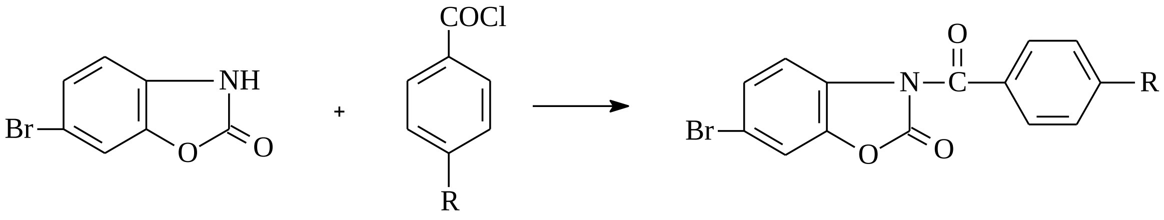
Compound	**The catalyst**	**The mole rations of reagents I:II:Catalyst**	**The melting points, ^0C**	**Productivity, %**
III	$ZnCl_2$	1:1,5:0,0125	157-159	61,0
III	$FeCl_3{\cdot}6H_2O$	1:1,5:0,0125	157-159	68,3
III	IAA	1:1,5:0,0125	157-159	35,1
III	$AlCl_3$	1:1,5:1	-	-
III	$AlCl_3$	1:1,5:2	-	-
III	$AlCl_3$	1:1,5:3	157-159	12,0

Based on the results obtained, the catalysts used in the synthesis of 3-benzoyl-6-brombenzoxazoline-2-ons can be classified as:

$FeCl_3{\cdot}6H_2O$ > $ZnCl_2$ > IAA > $AlCl_3$

It is well known from this series that at the same time results of the reaction of 6-brombenzoxazolin-2-on (I) with benzoyl chloride, $FeCl_3{\cdot}6H_2O$ showed the highest activity, and $AlCl_3$ showed the lowest activity.

The reactions of 6-Brombenzoxazolin-2-on (**I**) substituted benzoic acid chloroangydrides (4-brom-, 4-nitro-, 4-methoxy-, 4-methylbenzoilchlorides) were carried out under the conditions found for benzoylation reaction. We performed these reactions by heating them in a nitrobenzole solution at 210-220 ^0C for 3 h in the presence of $1{,}25{\cdot}10^{-2}$ mole of $FeCl_3{\cdot}6H_2O$. As a result of the reactions, 3-aroil-6-brominebenzoxazoline-2-they (**Va-d**) were synthesized (Table 2).



I **IV a-d** **V a-d**

The structure of the synthesized 3-aroil-6-brombenzoxazoline-2-ones (**Va-g**) was confirmed using IR- and mass spectrometry methods.

Table 2. Physico-chemical properties of 3-aroil-6-brombenzoxazolin-2-on

№	R	The melting points ^0C	Productivity %	Mass-spektrum, m/z, M^+	The CO group in position 3
Va	4-Br	218-220	71	398-400	1650
Vb	4-NO_2	227-229	74	366	1665
Vc	4-CH_3O	275-277	55	351	1665
Vd	4-CH_3	136-138	52	333-335	1650

In the IR spectra of 3-aroil-6-brombenzoxazolin-2-on (**Va-d**), the unstable deformation of the 3-position carbonyl group absorption lines (1650-1680 sm^{-1}) and the 1,2,4-substituted benzene ring CH fragment can be observed at the absorption lines (805-825 and 870-885 sm^{-1}).

The mass spectra revealed the presence of the proposed 3-aroil-6-brombenzoxazolin-2-on (**Va-d**) peaks of molecular ions and fragments confirming their structure (Table 2).

The data in Table 2 show that the introduction of electron-receptor (Br, NO_2) in the aromatic nucleus of the acetylating agent, namely benzoic acid chlorangidides, increases the yield of 3-aroil-6-brombenzoxazolin-2 (**Va, b**).

This is due to the effect of the electron-receptor subunits (Br, NO_2) on the molecule to increase the carbon charge of the carbonyl group and to increase the reaction ability of the cationic acid as an electrophilic agent in the electrophilic reaction. On the contrary, it is possible to observe the decrease in the yield of 3-asetyl-6-brombenzoxazolin-2-ions (**Vc, d**) due to the introduction of electron-ion groups (CH_3, CH_3O) in the molecule.

Thus, we performed the synthesis of 3-aroil-6-brombenzoxazoline-2-on (**Va-d**) in the presence of $1{,}25 \cdot 10^{-2}$ mol of $FeCl_3 \cdot 6H_2O$.

EXPERIMENTAL PART

The progress of the reactions and the purity of the substances were monitored by thin-layer chromatography (TLC) (Silufol UB-254, reagent - iodine vapor or 1 g KMnO4 + 4 ml conc. H_2SO_4 + 96 ml H_2O).

The IR spectra of the substances were obtained on a KBr tablet on the UR-20 spectrometer.

Mass spectra were obtained by direct injection of the sample into the ion source MS 25-RF (Kratos) spectrometer (energy of ionizing electrons 70 eV, ion source temperature 250^0C, sample input temperature 200^0C).

Synthesis of 3-benzoil-6-brombenzoxazolin-2-on (III)

2.15g (0.01 mol) of 6-brombenzoxazolin-2-solution was dissolved in 20 ml of nitrobenzene in two-mouth tube, adding 2.1g (0.015 mol) of benzoilchloride and 0.03g (0.000125 mol) of $FeCl_3 \cdot 6H_2O$. The reaction mixture was boiled for 3 hours at $210\text{-}220^0C$ using a reversible refrigerant. After cooling, the reaction mixture was washed with 4% HCl, water with pH=7,5% $NaHCO_3$, and again with water pH=7. The solvent was evaporated with steam, the precipitated sediment was separated, rinsed with water, dried and recrystallized with benzene. 3-Benzoyl-6-bromobenzoxazolin-2-one was obtained 2.16 g (68%). Fluid temperature 157-159^{0}C, Rf = 0.44

The other 3-aroil-6-brombenzoxazolin-2 (**Va-d**) given in the table was obtained by the above method.

CONCLUSION

As a result of our research, 3-benzoyl-6-bromobenzoxazolin-2-one (**III**) was synthesized in the benzoylation reaction of 6-bromobenzoxazolin-2-one (**I**) with benzoyl chloride in the presence of $1{,}25 \cdot 10^{-2}$ of $ZnCl_2$, $FeCl_3 \cdot 6H_2O$, and iron acetylacetonate (IAA) catalysts in a nitrobenzene solvent at a temperature of 200-210^{0}C for 3 hours. According to the results of the simultaneous acylation reactions of 6-bromobenzoxazolin-2-one (**I**) with benzoyl chloride, it was found that $FeCl_3 \cdot 6H_2O$ exhibits the highest activity, and $AlCl_3$ exhibits the lowest activity.

We observed that the introduction of electron-withdrawing substituents (Br, NO_2) into the aromatic nucleus of benzoic acid chlorides increases the yield of 3-aroyl-6-bromobenzoxazolin-2-ones (**Va,b**), while the introduction of electron-donating groups (CH_3,CH_3O) into the molecule decreases the yield of 3-acyl-6-bromobenzoxazolin-2-ones (**V v,g**). Thus, we carried out the synthesis of 3-aroyl-6-bromobenzoxazolin-2-ones (**Va-g**) in the presence of $1{,}25 \cdot 10^{-2}$ mol of $FeCl_3 \cdot 6H_2O$.

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