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# CATALYTIC ACYLATION OF BENZOXAZOLIN-2-ONES IN THE PRESENCE OF ZINC CHLORIDE

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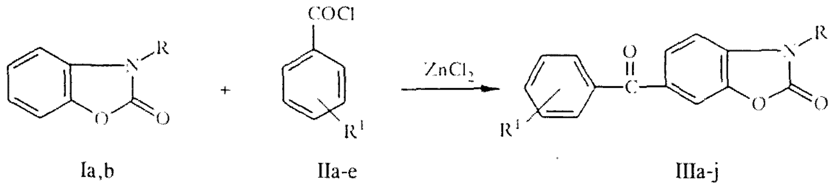
*In the acylation of benzoxazolin-2-ones by aromatic acid chlorides in the presence of* $10^{-2}$ *mole of* $ZnCl_2$*, the yields of the corresponding 6-aroylbenzoxazolin-2-ones depend on the electronegativity of the acylating agent and the nucleophilicity of the benzoxazolin-2-ones.*

The known methods for synthesizing 6-acylbenzoxazolin-2-ones are based on acylation of benzoxazolin-2-ones by carboxylic acid chlorides, using a large excess (3-4 moles) of anhydrous $AlCl_3$ [1, 2]. However, these reactions have serious disadvantages, such as the need for working with the corrosive and hygroscopic $AlCl_3$, as well as the exothermic decomposition by water and the process of washing out the inorganic salts. A further disadvantage is that under these reaction conditions, aromatic acid chlorides do not react with benzoxazolin-2-ones [2].

We had previously demonstrated the feasibility of benzoylation of benzoxazolin-2-ones in the presence of small quantities of $ZnCl_2$ [3]. In the work reported here, we investigated the catalytic acylation of benzoxazolin-2-ones by aromatic acid chlorides.

The properties and yields of the products obtained under optimal conditions — the corresponding 6-aroylbenzoxazolin-2-ones (IIIa-j) — are listed in Table 1.



Ia) R = H, b) R = Me; IIa) $R^1$ = H, b) $R^1$ = 3-Br, c) $R^1$ = 4-$NO_2$, d) $R^1$ = 3-Me, e) $R^1$ = 4-OMe; IIIa) R = $R^1$ = H; b) R = H, $R^1$ = 3-Br; c) R = H, $R^1$ = 4-$NO_2$; d) R = H, $R^1$ = 3-Me; e) R = H, $R^1$ = 4-OMe; f) R = Me, $R^1$ = H; g) R = Me, $R^1$ = 3-Br; h) R = Me, $R^1$ = 4-$NO_2$; i) R = Me, $R^1$ = 3-Me; j) R = Me, $R^1$ = 4-OMe

With the aim of defining the optimal conditions for the acylation and determining the limits on the use of small quantities of catalyst, we investigated the influence of the quantity of $ZnCl_2$, the reaction temperature, and the reaction time on the product yield in the benzoylation of 3-methylbenzoxazolin-2-one (Ib).

The best yield of 6-benzoyl-3-methylbenzoxazolin-2-one (IIIf) was obtained with a ratio Ib:IIa:$ZnCl_2$ = 1:1.2:$10^{-2}$, and with heating the reaction mass for 3 h at 200-210°C. The use of larger amounts of catalyst did not increase the yield of IIIf, while a reduction of the catalyst quantity to $10^{-4}$ mole reduced the yield of IIIf to the point where only traces were found.

It is known that the successful accomplishment of acylation reactions depends on the activity of the acylating agent. Usually, with increasing electronegativity of the acylating agent, the activity increases [4-6]; other data, however, indicate the exact opposite [7, 8].

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TABLE 1. Physicochemical Characteristics of Synthesized Compounds

| Compound | Empirical formula | mp, °C (and solvent) | Values of m/z of ions (and relative intensity, %) | | | IR spectrum, $\nu$, cm$^{-1}$, C=O | Yield, % |
|---|---|---|---|---|---|---|---|
| | | | $M^+$ | $A^+$ | $B^+$ | | |
| IIIa | $C_{14}H_9NO_3$ | 167...169* (benzene) | 239 (37) | 162 (100) | 77 (18) | 1680, 1770, 3480 | 60 |
| IIIb | $C_{14}H_8BrNO_3$ | 214...216 (ethanol) | 317/319 (42) | 162 (100) | 155/157 (28) | 1650, 1775, 3450 | 66 |
| IIIc | $C_{14}H_8N_2O_5$ | 227...229 (ethanol) | 284 (43) | 162 (100) | 122 (21) | 1665, 1785, 3500 | 72 |
| IIId | $C_{15}H_{11}NO_3$ | 203...205 (ethanol) | 253 (37) | 162 (100) | 91 (24) | 1650, 1780, 3450 | 48 |
| IIIe | $C_{15}H_{11}NO_4$ | 275...277* (ethanol) | 269 (32) | 162 (100) | 107 (27) | 1650, 1770, 3450 | 45 |
| IIIf | $C_{15}H_{11}NO_3$ | 145...147* (ethanol) | 253 (29) | 176 (100) | 77 (31) | 1680, 1770, — | 74 |
| IIIg | $C_{15}H_{10}BrNO_3$ | 136...138 (ethanol) | 331/333 (35) | 176 (100) | 155/157 (28) | 1650, 1775, — | 80 |
| IIIh | $C_{15}H_{10}N_2O_5$ | 155...157 (acetonitrile) | 298 (34) | 176 (100) | 122(23) | 1665, 1780, — | 85 |
| IIIi | $C_{16}H_{13}NO_3$ | 148...150 (ethanol) | 267 (28) | 176 (100) | 91 (26) | 1650, 1775, — | 68 |
| IIIj | $C_{16}H_{13}NO_4$ | 178...180 (acetonitrile) | 283 (30) | 176 (100) | 107 (32) | 1650, 1780, — | 62 |

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*Constants of compounds are identical to those reported in [9, 10].

Our investigation showed that the introduction of electron-acceptor substituents ($NO_2$, Br) into the ring of the acylating agent resulted in higher yields of the corresponding compounds III, while the introduction of electron-donor substituents (Me, MeO) resulted in lower yields of the corresponding compounds III. It should also be noted that the yields of the acylation products are higher in the case of 3-methylbenzoxazolin-2-one (Ib) than with the unsubstituted benzoxazolin-2-one (Ia).

The structures of the synthesized compounds IIIa-j were proven by means of IR spectroscopy, mass spectrometry, elemental analysis, and a comparison of the constants of previously synthesized compounds with the values reported in the literature [9, 10].

The mass spectra of compounds IIIa-j, regardless of the nature of R and $R^1$, are all monotypical in terms of the direction of fragmentation (Table 1), which consists of rupture of the Ar—CO bond to form fragments A ($M^+$ − Ar) and B (Ar). Other directions of fragmentation involving elimination of the heterocyclic system do not contribute significantly.

It should be noted that the introduction of donor (+M) and acceptor (−M) substituents into the ring of the aroyl residue shifts the IR absorption maximum for stretching vibrations of the carbonyl group in position 6 of the benzoxazolin-2-one in the direction of lower frequencies, the shift amounting to 20-30 cm$^{-1}$ relative to 6-benzoylbenzoxazolin-2-ones (IIIa-f); this indicates donor−acceptor interaction of the carbonyl group in position 6 with the substituents of the aroyl residue.

## EXPERIMENTAL

The IR spectra of the compounds were recorded on a UR-20 spectrometer in KBr tablets. The mass spectra were obtained in a Kratos MS 25-RF instrument with direct introduction of the sample into the ion source, ionizing electron energy 70 eV, ion source temperature 250°C, temperature of sample introduction system 200°C. The course of the reaction and the individuality of the synthesized compounds were monitored by means of TLC on Silufol UV-254 plates in a benzene−ethanol solvent system (21:2), developer 1 g $KMnO_4$ + 4 ml $H_2SO_4$ + 96 ml $H_2O$.

Elemental analyses of the compounds for C, H, and N were consistent with the calculated values.

3-Methylbenzoxazolin-2-one (Ib) was obtained by a method given in [11].

**6-Benzoylbenzoxazolin-2-one (IIIa).** A mixture of 1.35 g (10 mmoles) of benzoxazolin-2-one, 1.68 g (12 mmoles) of benzoyl chloride, and 0.0136 g (0.1 mmole) of $ZnCl_2$ in 15 ml of nitrobenzene was heated for 3 h at 200-210°C. The solvent was removed by steam distillation; the residue was filtered, washed with water, and dried, obtaining 1.43 g (60%) of compound IIIa.

The other 6-aroylbenzoxazolin-2-ones that are listed in Table 1 (IIIb-j) were synthesized by analogous procedures.

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