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SHORT COMMUNICATION

$FeCl_3$-DMF COMPLEX AS EFFICIENT CATALYST FOR THE SYNTHESIS OF 6-ACYL-2(3*H*)-BENZOXAZOLONES AND 6-ACYL-2(3*H*)-BENZOTHIAZOLONES

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ABSTRACT. $FeCl_3$-DMF complex has been tested on Friedel-Crafts reaction of 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone with acid chlorides and anhydrides as acylating agents. In these conditions, the 6-acyl-2(3*H*)-benzoxazolones and 6-acyl-2(3*H*)-benzothiazolones were obtained in yields ranging from 52 to 89%. Among the various commonly catalysts; $AlCl_3$-DMF, $ZnCl_2$-DMF and PPA, explored in this study, the best conditions using $FeCl_3$-DMF were found the most convenient one

KEY WORDS: $FeCl_3$-DMF, $AlCl_3$-DMF, $ZnCl_2$-DMF, PPA, 6-Acyl-2(3*H*)-benzothiazolones, 6-Acyl-2(3*H*)-benzothiazolones

INTRODUCTION

The 6-acyl-2(3*H*)-benzoxazolones and 6-acyl-2(3*H*)-benzothiazolones derivatives, in particular are interesting, with anti-inflammatory, analgesic, antiepiliptic and antiviral properties. They are important building block in organic synthesis and in the design of new pharmacophores [1-15]. Due to their wide range of application, the syntheses of these derivatives by Friedel-Crafts acylation reaction have received great deal of attention [16-23]. In the literature, the most straight forward protocols using polyphosphoric acid (PPA), and Lewis acids such as aluminium chloride ($AlCl_3$) and zinc chloride ($ZnCl_2$) in *N,N*-dimethylformamide (DMF) as solvent, with carboxylic acids, acid chlorides or anhydrides have been reported [24-29].

Moreover, the Friedel-Crafts acylation using these conditions, generally involve the use of a large excess of catalysts and after aqueous work-up a large of amount of toxic waste is generated [24-29]. During recent years, the ferric chloride ($FeCl_3$) catalyst has been used as a catalyst in several organic transformations with excellent yields and great regioselectivity due to its low cost, ease of use, and environmental friendly properties [30-38]. On the other hand, it has been known that ferric chloride forms a complex with *N,N*-dimethylformamide by interaction with the carbonyl oxygen [39]. Previously, we reported the I_2-*N,N*-dimethylformamide complex as useful catalyst in the Friedel-Crafts acylation of aromatic substrates [40]. In the work reported here, we use the ferric chloride-*N,N*-dimethylformamide complex ($FeCl_3$-DMF) as a potential catalyst in the Friedel-Crafts acylation of 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone substrates with acid chlorides and anhydrides as acylatings agents for the first time.

EXPERIMENTAL

All reactions were monitored by thin layer chromatography using Merck TLC silica gel 60 F_{254}. Melting points were measured in open capillary tubes on an Electro thermal-apparatus. The IR spectra were obtained on a Perkin-Elmer 457 spectrometer using KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Brucker 400 spectrometer using DMSO-D_6 or $CDCl_3$ as solvent and (TMS) as an internal standard.

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General procedure using $FeCl_3$-DMF complex for the acylation of 2(3H)-benzoxazolone and 3-methyl-2(3H)-benzoxazolone. A mixture of $FeCl_3$ (38.92 g, 0.24 mol) and DMF (4.7 mL, 0.066 mol) were placed in a three neck round bottom flash (250 mL). The flask was then equipped with a reflux condenser with a $CaCl_2$ tube, and a mechanical stirrer. The flash was then placed in a oil bath thermostated at 90 °C. (0.04 mol) of 2(3*H*)-benzoxazolone or 3-methyl-2(3*H*)-benzoxazolone was added in portions. When the mixture was uniformly mixed, (0.06 mol) of acid chloride or acid anhydride was then added dropwise, and the temperature was subsequently raised to 170 °C under stirring for 3 hours. The products were isolated by addition of ice water. The precipitate was stirred for 1 h, collected by filtration, dried and crystallized.

General procedure using $FeCl_3$-DMF complex for the acylation of 2(3H)-benzothiazolone and 3-methyl-2(3H)-benzothiazolone. A mixture of $FeCl_3$ (38.92 g, 0.24 mol) and DMF (4.7 mL, 0.066 mol) were placed in a three neck round bottom flash (250 mL). The flask was then equipped with a reflux condenser with a $CaCl_2$ tube, and a mechanical stirrer. The flash was then placed in a oil bath thermostated at 90 °C. (0.04 mol) of 2(3*H*)-benzothiazolone or 3-methyl-2(3*H*)-benzothiazolone was added in portions. When the mixture was uniformly mixed, (0.06 mol) of acid chloride or acid anhydride was then added dropwise, and the temperature was subsequently raised to 170 °C under stirring for 3 hours. The products were isolated by addition of ice water. The precipitate was stirred for 1 h, collected by filtration, dried and crystallized. The present products demonstrate the procedure.

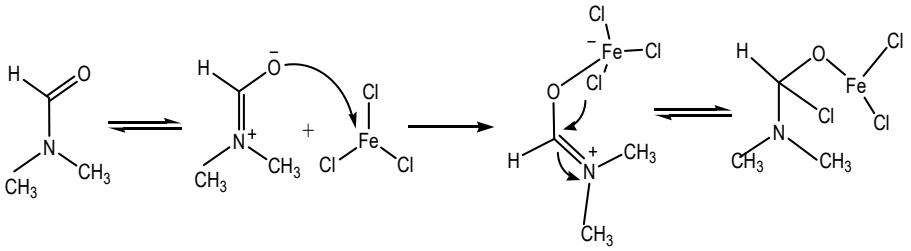
6-Benzoyl-2(3H)-benzoxazolone (3). Yield: 72%; m.p. 169-170 °C; IR (KBr, cm^{-1}) ν: 3140 (NH), 1780 (CO), 1640 (CO); 1610 (C=C). ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.22 (d, 1H, H-4, J = 7.99 Hz), 7.54-7.72 (m, 7H, H-5, H-7, C_6H_5), 12.07 (s, 1H, NH); ^{13}C-NMR (DMSO-d_6, 400 MHz): 107.75, 108.81, 125.74, 126.95, 127.84, 129.31, 130.76, 133.22, 135.89, 141.67 (aromatic carbons**)**, 152.82 (CO), 192.82 (CO).

6-Benzoyl-2(3H)-benzothiazolone (13). Yield: 74%; m.p. 216-217°C; IR (KBr, cm^{-1}) ν: 3240 (NH), 1667 (CO), 1638 (CO), 1618 (C=C). ^{11}H-NMR (DMSO-d_6, 400 MHz) δ: 7.24 (d, 1H, H-4, J = 7.88 Hz, C_6H_3), 7.70-7.95 (m, 7H, H-5, H-7, C_6H_5), 12.19 (s, 1H, NH); ^{13}C-NMR (DMSO-d_6, 400 MHz): 111.35, 123.61, 124.84, 128.61, 128.96, 129.41, 131.38, 132.32, 137.37, 140.22 (aromatic carbons), 170.34 (CO), 198.71 (CO).

RESULTS AND DISCUSSION

In order to optimize the experimental conditions, the activity of $FeCl_3$-DMF catalyst was first explored in the acylation of 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone, with benzoyl chloride. Using the $FeCl_3$-DMF complex, after various attempts, 6-benzoyl-derivatives were obtained with 68 and 69% yields at 170 °C after 3 hours. It is also mentioning that, the best yields were obtained when the amount of $FeCl_3$ was in the range of 6 equivalents with respect to 0.1 mol equivalent of 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone and 0.15 equivalent of benzoyl chloride as acylating agent.

It is clear that the $FeCl_3$ cannot be considered, in such conditions, as a catalyst. It is previously reported that in the Friedel-Crafts acylation using $AlCl_3$-DMF catalyst, the formation of a complex between $AlCl_3$, *N,N*-dimethylformamide involving the π and the n electrons of the heterocycles [25-27]. In these conditions, 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone can be acylated only when the amount of $AlCl_3$ was in the range of 7-11 equivalents [25-27]. As illustrated in Scheme 1, we propose a mechanism which is a complex formation of $FeCl_3$-DMF. When dissolved in DMF, $FeCl_3$ has the possibility to interact with the oxygen atom to generate equilibration between the free species and the Lewis salt stabilized by mesomery.

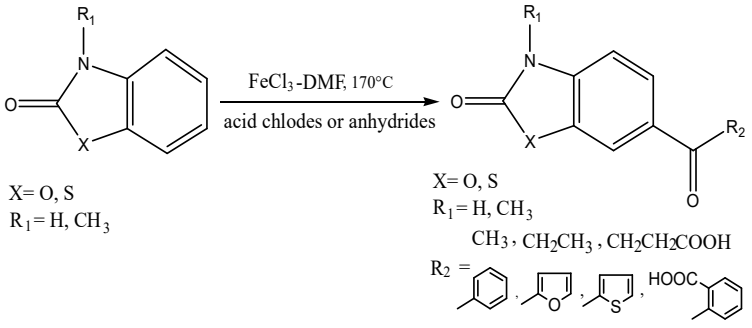


Scheme 1. Proposed mechanism of $FeCl_3$-DMF complex formation.

Table 1. 6-Acyl-2(3*H*)-benzoxazolones and 6-acyl-2(3*H*)-benzothiazolones derivatives under optimized conditions.

Compound	X	R_1	R_2	M.p. (°C)[a]	Yield[b]
1	O	H	CH_3	227-228	68
2	O	CH_3	CH_3	167-168	73
3	O	H	C_6H_5	169-170	72
4	O	CH_3	C_6H_5	147-148	86
5	O	H	2-C_4H_3O	233-234	63
6	O	CH_3	2-C_4H_3O	140-141	77
7	O	H	CH_2CH_2COOH	218-219	52
8	O	CH_3	CH_2CH_2COOH	179-180	63
9	O	H	2-COOH-C_6H_5	243-244	53
10	O	CH_3	2-COOH-C_6H_5	210-211	58
11	S	H	CH_3	190-191	69
12	S	CH_3	CH_3	145-146	75
13	S	H	C_6H_5	216-217	74
14	S	CH_3	C_6H_5	147-148	89
15	S	H	2-C_4H_3S	223-224	62
16	S	CH_3	2-C_4H_3S	124-125	69
17	S	H	CH_2CH_2COOH	241-242	56
18	S	CH_3	CH_2CH_2COOH	226-227	68
19	S	H	2-COOH-C_6H_5	236-237	55
20	S	CH_3	2-COOH-C_6H_5	221-222	60

[a]Melting point. [b]Isolated yield after crystallization.



Scheme 2. Acylation of 2(3*H*)-benzoxazolone, 2(3*H*)-benzothiazolone using $FeCl_3$-DMF catalyst.

As shown in Table 1, we have exemplified the versality of our catalyst for different cases. Good to excellent yields were observed. It should also be noted that the yields of N-methyl-derivatives are higher than for 2(3*H*)-benzothiazolone and 2(3*H*)-benzoxazolone. This may be probably due to the hydrogen mobility of the heterocycles [23]. Using these conditions, we have produced a number of 6-acyl-2(3*H*)-benzoxazolones and 6-acyl-2(3*H*)-benzothiazolones using acid chlorides and anhydrides (Scheme 2).

The efficiency and applicability of these conditions were compared with reported methods commonly used for the preparation of 6-acyl-derivatives (Table 2) [24-27, 29]. As Table 2 demonstrates, the behavior of 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone in the presence of $FeCl_3$-DMF catalyst appears to be parallel to that in the case of $AlCl_3$-DMF catalyst and in our method which afforded the best results [24-29]. We have exemplified the versality of our catalyst for different cases. Good to excellent yields were observed for aliphatic and aromatic acid chlorides or anhydrides.

These results can probably due to the rate of formation of the complex $FeCl_3$-DMF in the initial stage was greater for $FeCl_3$ due to its high melting point and its simple decomposition complex witch permit the reactive intermediate to be formed under the reaction conditions compared with other Lewis acids used.

Table 2. The comparative yields of 6-acyl-derivatives using the present method versus the reported methods.

Compound	X	R_1	R_2	Comparative yields (%)			
				PPA[a]	$AlCl_3$-DMF[b]	$ZnCl_2$-DMF[c]	$FeCl_3$-DMF
1	O	H	CH_3	62	65	59	68
2	O	CH_3	CH_3	63	70	67	73
3	O	H	C_6H_5	58	67	65	72
4	O	CH_3	C_6H_5	69	76	73	86
5	O	H	2-C_4H_3O	-	61	58	63
6	O	CH_3	2-C_4H_3O	-	71	58	77
7	O	H	CH_2CH_2COOH	-	48	23	52
8	O	CH_3	CH_2CH_2COOH	-	61	32	63
9	O	H	2-COOH-C_6H_5	-	49	24	53
10	O	CH_3	2-COOH-C_6H_5	-	53	33	58
11	S	H	CH_3	61	66	60	69
12	S	CH_3	CH_3	65	73	69	75
13	S	H	C_6H_5	65	69	63	74
14	S	CH_3	C_6H_5	72	79	75	89
15	S	H	2-C_4H_3S	-	58	49	62
16	S	CH_3	2-C_4H_3S	-	62	58	69
17	S	H	CH_2CH_2COOH	-	52	29	56
18	S	CH_3	CH_2CH_2COOH	-	58	39	68
19	S	H	2-COOH-C_6H_5	-	51	47	55
20	S	CH_3	2-COOH-C_6H_5	-	55	44	60

Methods: (a) PPA (120 g), carboxylic acids (0.06 mol), 3 h, 100 °C. (b) $AlCl_3$ (0.36 mol) in 7.1 mL of DMF, acid chlorides or anhydrides (0.06 mol), 3 h, 85 °C ; (c) $ZnCl_2$ (0.32 mol) in 6.25 mL of DMF, acid chlorides or anhydrides (0.06 mol), 3 h, 135 °C.

CONCLUSION

We developed an efficient method using $FeCl_3$-DMF complex for the acylation of 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone. This reaction take place at 170°C with a variety of acid chlorides or anhydrides to yield 6-acyl-2(3*H*)-benzoxazolones and 6-acyl-2(3*H*)-benzothiazolones in excellent yields rangring from 52 to 89%.

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