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SHORT COMMUNICATION

CHEMOSELECTIVE *C*-BENZOYLATION OF PHENOLS BY USING $ALCl_3$ UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT. Substituted phenols were chemo-selectively reacted with benzoylchloride in presence of aluminum chloride under solvent-free condition to afford the corresponding 2'-hydroxy aryl benzophenones in excellent yields (72-96%). Naphthol benzoylation resulted in lower yields as compared to phenols. Both reactions completed in 5-10 min with quantitative yields providing excellent control over regioselectivity of products.

KEY WORDS: Chemoselective C-acylation, F-C reaction, Fries rearrangement

INTRODUCTION

Friedel-Crafts acylation and benzoylation reactions are of great important in both academic research and industrial processes to synthesize aromatic ketones [1, 2]. Traditional Friedel-Crafts acylation or benzoylation reactions employ acid chlorides and Lewis acids ($AlCl_3$ [3], $ZnCl_2$ [4], $BiCl_3$ [5], $FeCl_3$ [6]) or Brønsted acid [7] with aromatic compounds. Hydroxyaryl ketones [8] are versatile intermediates in the synthesis of biologically active chalcones [9] flavones [10], pyrazolines [11], and indazoles [12]. O-hydroxydiaryl ketones exhibit protein kinase B inhibitor [13], cyclin-dependent kinase inhibitor [14] and cysteine protease modulator activities [15]. 4'-Hydroxy and 2'-hydroxypropiophenone are used as intermediates in manufacturing perfumes, pharmaceuticals and as UV adsorbents [1]. Hydroxydiaryl ketone moieties occur in natural products such as cotoin [16], balanol [17] and daunorubicin [18] or they are used as building blocks for the synthesis of various pharmaceutical compounds.

In this work, benzoylation of phenolic compounds was carried out following the two steps of O-benzoylation and then Fries rearrangement of aryl benzoates (Scheme 1). Fries rearrangement employs using anhydrous $AlCl_3$ [19], CH_3SO_3H [20], $Bi(OTf)_3$ [21], $ZrCl_4$ [22], Zeolite H-beta [23]. Direct Friedel-Crafts acylation of phenols using acetyl chloride (chemoselective reaction) has been done by $Bi(OTf)_3$ [21] or $Hf(OTf)_4$ [24] in PhMe-$MeNO_2$ as solvent at 110 ^oC for 5-6 h in moderate yield (64-69%) and $Sc(OTf)_3$ in $LiClO_4$-$MeNO_2$ at 50 ^oC for 6 h into 62% yield [25a]. Furthermore *ortho* and *para* propionylation of simple phenols was carried out by propionylchloride in presence of Zeolite H-beta [23] as catalyst under solvent free condition at 140 ^oC for 6 h in 81% yield, and benzoylation of anisole was achieved by benzoylchloride in presence of B_2O_3-ZrO_2 in nitro benzene as solvent at 150 ^oC for 22 h [25b] or by I_2-DMF at 140 ^oC for 12 h in 67% [25c]. To the best of our knowledge there is no previous report for direct C-benzoylation of phenols and naphthol using $AlCl_3$ under solvent free conditions. The use of aluminum chloride is significant because, it has low cost, commercially available, easy to handle and easy of work-up. On the other hand, avoiding the solvent reduces number of components in reaction, stops any solvent emission problems, and gets around any solvent recycling requirements. Herein we describe a Friedel-Craft benzoylation of substituted phenols, through a modified benzoylation procedure that gives O-substituted benzophenones regioselectively with excellent yields. The objective of the present work is elimination of esterification step (step 1,

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Scheme 1) in conjunction with absence of solvent, e.g. nitrobenzene, toluene, dichloromethane, nitro methane, etc., and low reaction time.

EXPERIMENTAL

^{1}H-NMR (300 MHz) spectra were recorded on a Varian VXR 300 instrument at 293 ^{o}K in $CDCl_3$. Chemical shift values were recorded in δ units (ppm) relative to Me_4Si as internal standard. Melting points were determined by using a Buchi melting point apparatus. Infrared spectra (IR) were recorded using KBr pellets on a Perkin-Elmer 240C analyzer. Thin layer chromatography (TLC) was performed on silica gel 60 PF254 plates or aluminum oxide plates from Merck.

Procedure for benzoylation of substituted 4-chlorophenol. To a mixture of 4-chlorophenol (7.8 mmol, 1 g) and anhydrous $AlCl_3$ (9.3 mmol, 1.24 g) stirred at 110 °C, benzoyl chloride (9.3 mmol, 1.31 g) was added in several portions, very carefully holding the temperature under 110 ^{o}C. After completion, the mixture was poured into ice water and then concentrated HCl (2-4 mL) was added subsequently. The suspension was stirred vigorously for 5-10 min. The crude desired products were obtained as yellow solids, after filtration crude product was purified by crystallization in ethanol/methanol and yield of product was recorded as 93%.

5-Chloro-2-hydroxyphenyl)(phenyl)methanone (Table 2, Entry 1). Color; yellow solid, m.p. 97-99 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 11.91 (s, D_2O exchangeable, 1H) 7.036 (d, J = 9 Hz, 1H) 7.56 (s, 1H) 7.46 (d, J = 2.4 Hz, 1H) 7.67 (d, J = 6.8 Hz, 2H) 7.51 (t, J = 6.2 Hz, 1H) 7.37 (d, J = 2.8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$); 200.56, 161.65, 137.15, 136.14, 132.36, 129.10, 128.55, 123.34, 120.05, 119.69.

(3,5-Dichloro-2-hydroxyphenyl)(4-methoxyphenyl)methanone (Table 2, Entry 3). White solid, Yield: 88%, m.p. 111-113 ^{o}C; IR: 1690, 3460 cm^{-1}, ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 12.44 (s, 1H, D_2O exchangeable), 6.88 (s, 1H) 7.32 (s, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.2 (d, J = 7.8 Hz, 2H), 2.31 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 183.0, 154.1, 154.0, 132.9, 131.1, 128.8, 128.4, 127.6, 124, 129, 127.9, 20.0.

(2-Hydroxy-5-methylphenyl)(phenyl)methanone (Table 2, entry 4). Yellow liquid; ($C_{14}H_{12}O_2$); mp: 81-83 ^{o}C; IR: 1695, 3398 cm^{-1}, ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 2.47 (s, 3H) 6.71(d, J = 8.1 Hz, 1H) 6.89 (d, J = 6.78 Hz, 2H) 7.1 (d, J = 8.4 Hz, 1H) 7.27(d, J = 8.1 Hz, 1H) 7.49-7.45 (m, 3H) 12.15 (s, 1H).

(3,5-Dichloro-2-hydroxyphenyl)(phenyl)methanone (Table 2, entry 6). Yellow solid, m.p. = 97-99 ^{o}C, IR; 1698, 3214 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6), δ = 10.6 (s, 1H) 8.15 (d, J = 7.8Hz, 2H), 7.77(d, J = 7.2Hz, 2H), 7.628 (t, 2H) 7.54 (s, 1H); ^{13}C-NMR (300 MHz, DMSO-d_6), δ = 218.0, 163.9, 145.9, 134.9, 131.5, 130.2, 129.8, 129.6, 129.4, 128.9, 127.9, 127.4, 125.9.

Procedure for benzoylation of 1-naphtol [26]. To a mixture of 1-naphthol (7 mmol, 1 g) and anhydrous $AlCl_3$ (10 mmol, 1.38 g) stirred at 50 ^{o}C, benzoyl chloride (10 mmol, 1.46 g) was added in several portions, very carefully holding the temperature under 50 °C. After completion, the mixture was poured into ice water and then concentrated HCl (2-4 mL) was added subsequently. The suspension was stirred vigorously for 5-10 min. The crude desired products were obtained as yellow solids after filtration crude product was purified by crystallization in ethanol/methanol and yield of product was recorded as 55%.

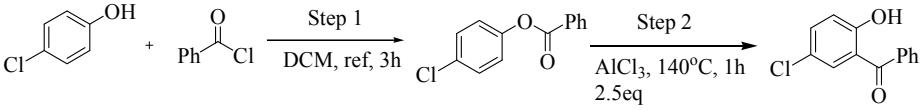
(1-Hydroxynaphthalen-2-yl)(phenyl)methanone (Table 3, Entry 1) [27]. Yellow solid; m.p. 72-74 ^{o}C; IR 3020, 1630, 1600, 1570 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6 13.92 (s, 1 H), 8.54 (m, 1H), 7.42-7.79 (m, 10H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 201.4, 163.9, 138.2, 137.3, 131.6, 130.3, 129.1, 128.3, 127.4, 125.9, 125.8, 124.5, 117.9, 112.5.

(2-Hydroxynaphthalen-1-yl)(phenyl)methanone (Table 3, Entry 2) [28]. White solid; m.p. = 74-76 ^{o}C, IR: 3350, 1647; ^{1}H NMR (300 MHz, $CDCl_3$): 7.14 (t, J = 8.0Hz, 1H), 7.33-7.21 (m, 3H), 7.40 (t, J = 7.56 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 13.10 (s, 1H).

(2-Methoxyphenyl)(phenyl)methanone (Table 3, Entry 5) [29]. Yellow solid, m.p. = 57-59 ^{o}C, IR 3354, 1650, 2918 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.72 (s, 3H), 6.99-7.05 (m, 2H), 7.36 (dd, J = 1.7, 7.5 Hz, 1H), 7.41-7.49 (m, 3H), 7.55 (m, 1H), 7.81 (dd, J = 1.25, 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.6, 111.5, 120.5, 128.2, 128.9, 129.6, 129.9, 131.9, 133.0, 127.8, 157.4, 196.5.

RESULT AND DISCUSSION

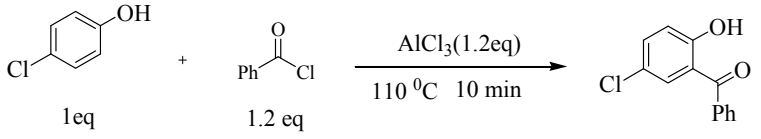
For comparison of *ortho*-benzoylation via conventional method and $AlCl_3$-solvent free initially, we attempted the C-benzoylation of *p*-chlorophenol **1**, as model reaction, via conventional method (Scheme 1). The *p*-chlorophenol was treated with benzoyl chloride **2** in dichloromethane at reflux for three hours (Scheme 1, step 1). After extraction (with DCM and dil. NaOH for removing of unreacted phenol), 4-chlorophenyl benzoate **3** was obtained. Fries rearrangement of **3** was accomplished by 2.5 equiv $AlCl_3$ at 140 ^{o}C for one hour (Scheme 1, step 2). After workup the 5-chloro-2-hydroxybenzophenone **4** was isolated. We calculated overall yield of step 1 and step 2, and it was obtained 64%.



1 **2** **3** **4**

Scheme 1. Preparation of hydroxyaryl ketones via conventional method.

Direct Friedel-Crafts of *p*-chlorophenol using benzoyl chloride and aluminum chloride under solvent free condition, was accomplished with different equivalent of $AlCl_3$ at the 100-110 ^{o}C temperature, which summarized in (Table 1) which the best condition was obtained by 1.2 equivalents $AlCl_3$ at 110 ^{o}C with 93% yield.

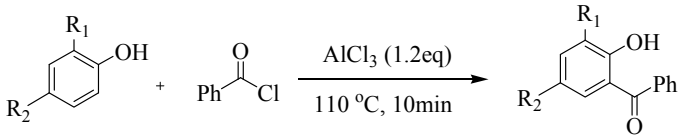


1eq 1.2 eq 93%

1 **2** **4**

In a typical procedure, 1 equivalent of *p*-chlorophenol and 1.2 equivalent aluminum chloride were mixed at room temperature. The mixture was heated at 110 ^{o}C (Scheme 2) followed by addition of 1.2 equivalents of benzoylchloride dropwise with grinding for 10 min. Then ice-

water was added slowly to quench the reaction. The solid product was isolated by filtration and recrystallized from methanol. The obtained yield was 93% (Table 2, entry 1). By these results, we found that for *C*-benzoylation of phenols, neither esterification step nor solvent needed. Furthermore, this method has excellent yield with low reaction time and easy to workup. A number of phenols have been converted to corresponding 2-hydroxy benzophenones (Table 2). The sterically hindered phenols, such as 2,4-dibromophenol 2-bromo-4-chlorophenols have also afforded to the desired benzophenone in excellent yields. As well as *p*-methoxy benzoylchloride reacted efficiently with 2,4-dichlorophenol and resulted into 81% yield. Interestingly, only 2-benzoyl-1-napthol **8** was obtained as a sole product by benzoylation of α-naphthol **7** in 50% yield, and 1-benzoyl-2-naphthol **10** also was formed from β-naphthol **9** at 45 ^{o}C in 55% yield (Scheme 3, Table 3).



5 **2** **6**

Scheme 2. C-benzoylation of substituted phenols using benzoyl chloride and $AlCl_3$ under solvent free condition.

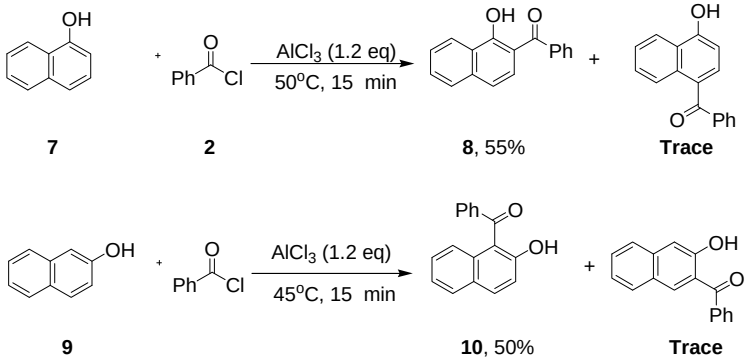
Table 1. Chemoselective benzoylation of *p*-chlorophenol in several equivalent of $AlCl_3$ at different temperatures.

Entry	Equiv $AlCl_3$	Temp. ^{o}C	Yield %
1	0.6	80	43
2	0.6	110	51
3	0.8	80	61
4	0.8	110	73
5	1.0	90	75
6	1.0	110	85
7	1.2	80	86
8	1.2	110	93

Table 2. Physico-chemical properties of 2-hydroxybenzophenone.

Entry	R_1	R_2	Ph	m.p. (^{o}C) (lit.)	Yield (%)
1	H	Cl	Ph	91 (93) [30]	93
2	H	Br	Ph	110 [31]	91
3	Cl	Cl	Ph	113 (115)	88
4	H	Me	Ph	81 (82) [32]	90
5	Br	Cl	Ph	80 (80) [30]	89
6	Br	Br	Ph	99 (99) [30]	88
7	H	OMe	Ph	80 (84) [33]	70
8	H	OH	Ph	146 [34]	70
9	Cl	Cl	4-$MeOC_6H_4$	110	75
10	Me	Me	Ph	38 [35]	78
11	OH	H	Ph	62	65
12	Me	H	4-$MeOC_6H_4$	-	78

Benzoylation of arenes by the above procedure such as toluene, benzene, bromobenzene, chlorobenzene anisole has been achieved in quantitative yield (Table 3). It is important that the benzoylation of these substrates was not possible with organo metallic reagents. The benzoylation of nitrobenzene resulted into lower yields of product, naphthalene and anthracene acylated at 30 ^{o}C in good yields. The major problem for the use of anhydrous $AlCl_3$ in F-C benzoylation with electron rich substrate is formation of the strong complexation with Lewis acids, which retard the progress of reaction. While in the presence of activated phenols, the reaction completes smoothly within ten minutes to give quantitative yields. On the other hand in conventional method, the amount of acid chlorides used are in excess than stoichiometric amount of Lewis acids are required while in the present procedure only stoichiometric amount of aluminum chloride and acid chlorides are used.



Scheme 3. Benzoylation of α- and β-naphthol.

Table 3. Physico-chemical properties of naphthyl benzophenone and aryl benzophenone by using benzoylchloride and $AlCl_3$ under solvent free condition.

Entry	Substrate	Yield %	Reported m.p. (^{o}C)
1	1-Naphthol	50	74 (73) [27]
2	2-Naphthol	55	76
3	Toluene	85	30 (18) [26]
4	Chlorobenzene	87	97 (96) [36]
5	Anisole	80	57 (61) [36]
6	1,2-Dichlorobenzene	85	104
7	Nitrobenzene	77	135 (136) [37]
8	Anthracene	72	142 (145) [38]
9	1-Chloro-2-nitrobenzene	90	102 (104) [39]

CONCLUSION

We have compared C-benzoylation of phenols by conventional method (esterification of phenols and Fries rearrangement of aryl benzoate) and direct C-benzoylation by $AlCl_3$ under solvent free condition. With this procedure, the benzoylation occurs chemoselectively at benzenoyd ring. Furthermore, the products were obtained with high degree of purity. The reaction completes just within 10 minutes, into excellent yield and avoid from solvent. This renew economical process will be useful for all those laboratories where organo metallic reagents are not accessible.

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