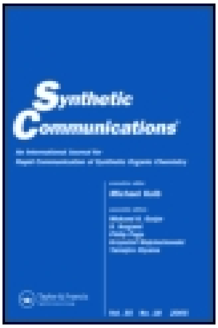

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Novel One-Pot Procedure for the Synthesis of 1,2-Diketones

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Abstract: A simple and convenient one-pot procedure is reported for the synthesis of 1,2-diketones from corresponding benzoin-type condensation reaction of aromatic aldehydes in water with *N,N*-dialkylbenzimidazolium salt as condensation catalyst and ferric chloride as oxidizing reagent.

Keywords: Benzils, benzimisazolium catalysts, benzoin condensation, 1,2-diketones

INTRODUCTION

Benzils have received a great deal of attention because of their applications as photosensitive reagents in photocurable coatings, as starting materials in organic and pharmaceutical synthesis,[1] and also as biologically active compounds.[2] Conventionally, benzils are prepared by several different methods, such as coupling of acid chlorides with SmI_2,[3] oxidation of mono ketones with SeO_2, and oxidation of acetylenes with $NaIO_4/RuO_2$,[4] $Tl(NO_3)_3$,[5] and $KMnO_4$.[6] Some organooxidants, such as 4-MeO-2,2,6,6-tetramethylpiperidinyl-l-oxy (TEMPO),[7a] (4-AcNH-TEMPO)-OTs-TsOH,[7b] 4-phCO_2-TEMPO,[7c] n-$Bu_4N[MoO(O)_2C_5H_4N(O)O_2)]$,[8] and H_2O_2-$[C_5H_5N(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)]_4\}$,[9] can also oxidize 1,2-diols to 1,2-diketones; however, these oxidants are complex and expensive. Meanwhile, benzils are able to be prepared by the oxidation of corresponding benzoins with inorganic oxidants such as $CuSO_4$/Py,

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Bi_2O_3/H^+, and HNO_3 in aq. solution[10] and RuO_4.[11] All these methods have drawbacks in terms of expensive regents, difficult reaction conditions, and low yields. Surprisingly, to our knowledge, there are no examples of simple synthesis of benzils directly from aldehydes in one pot. We report herein a simple and convenient procedure for the synthesis of a variety of benzils from corresponding aldehydes.

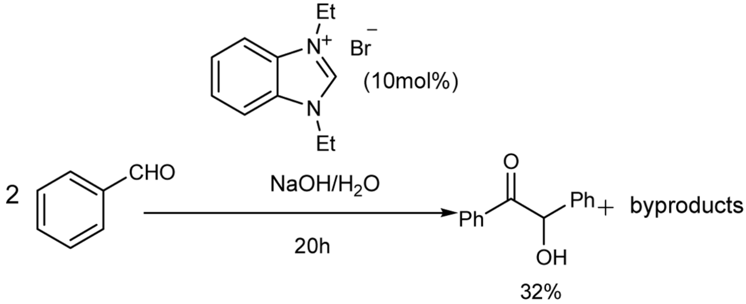
RESULTS AND DISCUSSION

In 2006, Iwamoto et al.[12] reported that benzion condensation reaction can be catalyzed by *N*,*N*-dialkylbenzimidazole in water to yield α-hydroxy ketones. We repeated this reaction and found that the yield of proucts is usually very low (Scheme 1).

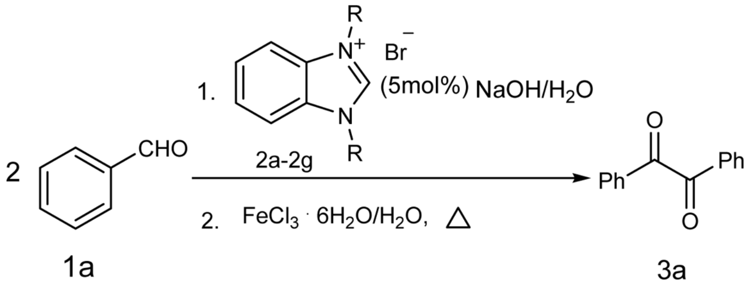
When we studied this reaction, it was found that one of the byproduct is benzils in the same system. Unfortunately, the yield of benzils was only 10% when the reaction was carried out in a nitrogen atmosphere. It can be concluded that in the reaction process, some of α-hydroxy ketones was oxidized in air to give benzil. Hence, It is possible to add one oxidant to the system and make the oxidation reaction complete. We chose $FeCl_3 \cdot 6H_2O$ as the oxidizing agent and directly added it into the reaction mixture after the catalytic benzoin condensation was finished. The good yield (71%) of the benzil was observed after workup.

To optimize the reaction condition, we examined this one-pot reaction by varying benzimidazolium salts, solvent, and time and using the reaction of benzaldehyde as a comparing reference (Scheme 2). The results are summarized in Tables 1 and 2.

From Table 1, it can be seen that as the number of the carbon atoms of the N-substituent increased from two to eight, the yields of benzil improved gradually. The yield was slightly reduced when the carbon



Scheme 1. Benzoin condensation catalyzed by benzimidazolium salt.



Scheme 2. Synthesis of benzils in one-pot reaction.

atom number increased to more than eight. So, 2e is the best catalyst in the reaction. We also found that the reaction takes place more smoothly than in the other organic solvent (Table 2).

Under optimized conditions (catalyzed by **2e** in water), the reactivity of a series of aromatic aldehydes in this reaction was examined; the results are summarized in Table 3. From the table it can be seen that aromatic aldehyde containing chloro-, bromo-, and methyl substituent afforded the desired benzils in higher yields. The reactions of 3-nitrobenzaldehyde or 4-nitrobenzaldehyde and *p*-hydroxyl benzaldehyde were considerably slow, and the yields of benzils were much lower. Furfural only gave furil in about 5% yield, mainly because of its easily oxidation by $FeCl_3$.

In conclusion, we developed a one-pot synthesis of benzils by the dimeric reaction of aldehydes with benzimidazolium salt as catalyst and ferric chloride as oxidant. This kind of reaction under the mild conditions opens a novel green entry to synthesis of benzils by a simple procedure.

Table 1. Synthesis of benzils catalyzed by benzimidazolium salts

Entry	Catalyst R	Time (h)	Yield (%)
1	CH_2CH_3	8	32
2	$CH_2CH_2CH_3$	8	55
3	$CH_2(CH_2)_2CH_3$	8	63
4	$CH_2(CH_2)_3CH_3$	8	72
5	$CH_2(CH_2)_6CH_3$	8	83
6	$CH_2(CH_2)_{10}CH_3$	8	82
7	$CH_2(CH_2)_{14}CH_3$	8	80

Table 2. Synthesis of benzils in different solvents

Entry	Solvent	Time (h)	Yield (%)
1	CH_3CH_2OH	24	67
2	CH_3OH	24	36
3	H_2O	24	83
4	THF	24	55

EXPERIMENTAL

Typical procedure for the synthesis of 1,2-diketones: Benzaldehyde **1a** (1.06 g, 10 mmol) was added to water (10 mL). To the mixture were added **2e** (0.5 mmol) and 10% NaOH aq (2.5 ml) under vigorous stirring. The reaction mixture was stirred for about 30 min at refluxing temperature. The solution was neutralized to pH = 5–6 by HOAc. Then 12 mmol $FeCl_3 \cdot 6H_2O$ were added into the solution. The solution was refluxed for another 7.5 h. The crude 1,2-diketone was obtained by extracted with ethyl acetate and concentrated in vaccuo. Pure 1,2-diketone was obtained by column chromatography (silica, hexane–EtOAc = 4:1) and characterized by IR and ^1H NMR spectral data. Their melting points were compared with authentic samples.

Table 3. Synthesis of benzils in one-pot reaction

					Mp (°C)	
Entry	Ar	Product	Time (h)	Yield (%)[a]	Found	Reported
1	Ph	3a	8	83	95–96	95–96
2	$4\text{-Me}-C_6H_4$	3b	24	75	103–105	103–105
3	$4\text{-MeO}-C_6H_4$	3c	24	70	130–131	131–132
4	$4\text{-OH}-C_6H_4$	3d	36	None	—	—
5	$4\text{-Cl}-C_6H_4$	3e	8	94	195–198	195–196
6	$3\text{-Br}-C_6H_4$	3f	8	86	122–124	—
7	$4\text{-Br}-C_6H_4$	3g	8	80	224–226	225–227
8	$4\text{-NO}_2-C_6H_4$	3h	36	Trace	—	—
9	$3\text{-Cl}-C_6H_4$	3i	8	90	114–116	116–117
10	$3\text{-NO}_2-C_6H_4$	3j	36	Trace	—	124–126
11	Furan-2-yl	3k	8	<5	165–166	167–168

[a] Isolated yields.

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