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SOLID STATE SYNTHESIS OF BENZILS AT LOW-HEATING TEMPERATURES

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Abstract : A simple and efficient method for the preparation of benzils through the solid state oxidation reaction of benzoins by $FeCl_3 \cdot 6H_2O$ at low-heating temperatures(80 ~ 90℃) is described. The oxidation conditions are mild. The products are easily separated with no pollutions produced.

Benzils have received a great deal of attention because of their practical applications, i.e. as a photosensative agent in photocurable coatings(1), and as a synthetic agent in organic and pharmaceutic synthesis. As we know, benzils are traditionally prepared by the oxidation of the corresponding benzoins with an oxidizing agent, such as $CuSO_4$/Py, Bi_2O_3/H^+, HNO_3 in an aqueous solution(2) and Ph_3PBr_2/MeCN, DMSO/$(COCl)_2/CH_2Cl_2$, $PhCH_2Et_3NBr_3/(PhCO)_2O_2$/MeCN, $Ti(OPr^i)_4$/THF, and $CrO_3 \cdot$

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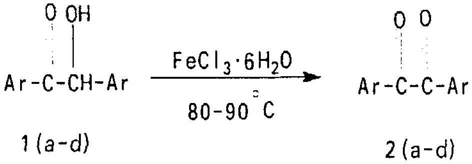
$(CH_3)_3N \cdot HCl / SiO_2$ in a nonaqueous solution(3). The available large number of "mild" oxidizing agents may be proven to be impracticable when the reactions are performed on a large scale. Also there are some problems associated with above syntheses, such as, severe conditions for the reaction, expensiveness and difficulty in preparing the reagent and separating the product from the reaction system, and serious environmental pollution.

Quite a few organic reactions proceed well in solid state. In some cases, the organic reaction occurs more efficiently in solid state than in solution phase(4,5). Here we report on how to prepare benzil and its derivatives from oxidation of the corresponding benzoin by $FeCl_3 \cdot 6H_2O$ in solid state at low-heating temperatures according to Scheme 1. A mixture of benzoin and $FeCl_3 \cdot 6H_2O$ was pulverized and kept at

Scheme 1 Oxidation of benzoins by $FeCl_3 \cdot 6H_2O$ in solid state



where Ar represents as follows: a. ph- ; b. p-Cl-ph- ; c. p-CH_3O-ph- ; d. p-CH_3-ph-.

80 ~ 90℃ for 4 hours, then washed with water. The pure product was collected with the yields of 89 ~ 95 % after filtration and purification, as shown in Table 1. It is clear that $FeCl_3 \cdot 6H_2O$

can act as a mild and extremely efficient oxidizing agent for the conversion of benzoin to the corresponding benzil in the absence of any solvent.

Table 1 Characterizations for compounds 2(a ~ d)

compound (formula)	melting point (lit.)/℃	yield / %	elemental analyses(cal.)/%		IR, υ_{max}/cm^{-1}	^{1}HNMR, δ /ppm
			C	H		
2a ($C_{14}H_{10}O_2$)	93 ~ 94.5 (94 ~ 95)(2a)	95.0	80.29 (79.99)	4.71 (4.79)	1658, 1592, 1578, 794, 717, 696, 681	7.16 ~ 8.10 (10H, m, Ar-H)
2b ($C_{14}H_8Cl_2O_2$)	196 ~ 197 (195 ~ 196)(7)	94.0	60.34 (60.24)	3.49 (2.89)	1661, 586, 880, 834, 734	7.45, 7.80 (8H, dd, Ar-H)
2c ($C_{16}H_{14}O_4$)	133 ~ 134 (131 ~ 133)(6)	89.5	71.69 (71.10)	5.10 (5.22)	1659, 1597, 1510, 799, 830	3.85 (6H, s, 2CH_3), 6.85, 7.85 (8H, dd, Ar-H)
2d ($C_{16}H_{14}O_2$)	102 ~ 104 (103 ~ 104)(6)	93.0	80.31 (80.65)	5.49 (5.92)	1660, 1595, 1570, 1450, 875, 830, 780, 740	2.41 (6H, s, 2CH_3), 7.25, 7.80 (8H, dd, Ar-H)

The yield of the synthesis reaction was affected by the reaction temperature. Table 2 shows the reaction yield at different temperature with the same reactant amounts (2.123g of **1a**, 8.110g of $FeCl_3 \cdot 6H_2O$) and reaction time (4 hours). Almost no benzil **2a** was produced at the temperature lower than 60 ℃,

Table 2 Yield of benzil 2a at different synthesis temperature

synthesis temperature* /℃	**60**	**70**	**75**	**80**	**90**
yield / %	nealy no product	**60**	**72**	**82**	**95**

* Total reaction time was 4 hours.

whereas an obvious reaction occurred at approximately 70℃. The yield of benzil gradually increased with the temperature and a nearly complete reaction was achieved at 90℃.

In conclusion, we have shown that the use of solid state reaction at low-heating temperatures provides an excellent method for oxidation reaction of benzoins with high yield. The procedure avoids the usage of organic solvent.

General Procedure

The general procedure adopted for the preparation of benzil **2a** is as follows. A mixture of benzoin **1a** (2.123g, 10 mmol) and $FeCl_3 \cdot 6H_2O$ (8.109g, 30 mmol) was finely powdered by an agate mortar and pestle at room temperature. The mixture was then transferred to a test tube and kept at 90 ℃ for 4 hours. After cooled down to room temperature, the reaction mixture was dissolved in 40 mL of water and filtrated. The obtained organic crystal was washed thrice with water, and a yellow crystal (m.p. 91 ~ 93 ℃) was collected. Recrystallization of the crude product from 95 % alcohol afforded a pure, faintly yellow needles benzil **2a** (1.998g, m.p. 93 ~ 94.5℃) in a yield of 95 % of the theoretical amount. The substituted benzils **2(b ~ d)** were synthesized at 80 ℃ for 4 hours. The IR and ^{1}HNMR for the products **2(a ~ d)** were consistent with the authentic specimens in the standard Sadtler Dada.

Experimental

$FeCl_3 \cdot 6H_2O$ and benzoin **1a** were of chemical grade and were used as received without further purification. The substituted benzoins **1b**, **1c**, and **1d** were prepared according to the procedures described in the litreature(8). Infrared spectroscopy of the products were recorded on an IRS66V FT-IR spectrometer with KBr disc and the values were tabulated in υ /cm^{-1}. ^{1}HNMR spectra were taken on a JEOL JNM-PMX-60SI spectrometer for solution in $CDCl_3$ with TMS as an internal reference, and the chemical shift values were given in δ /ppm. Elemental analyses were obtained by Perkin Elmer 240C. Melting points were measured on an X_4 micromelting point apparatus and all of them were uncorrected .

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