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OXIDATIVE COUPLING REACTIONS OF PHENOLS WITH $FeCl_3$ IN THE SOLID STATE

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ABSTRACT Some oxidative coupling reactions of phenols with $FeCl_3$ are faster and more efficient in the solid state than in solution. Some coupling reactions in the solid state are accelerated by irradiation with ultrasound. Some coupling reactions are achieved by using a catalytic amount of $FeCl_3$.

INTRODUCTION

Oxidative coupling of phenols are usually carried out by treatment of phenols in solution with more than equimolar amount of metal salts such as $FeCl_3$ or manganese tris(acetylacetonate), although the latter is too expensive to use in large quantities. The coupling reactions of phenols with $FeCl_3$, however, sometimes give quinones as byproducts. Recently, we found that the coupling reaction with $FeCl_3$ proceeds much faster and more efficiently in the solid state than in solution and that the reaction in the solid state is accelerated by irradiation with ultrasound. We also found that the coupling reaction in the solid state can be achieved by using a catalytic amount of $FeCl_3$.

EXPERMENTAL AND DISCUSSION

A mixture of **1** (1 g, 7 mmol) and $FeCl_3 \cdot 6H_2O$ (reagent I, 3.8 g, 14 mmol) was finely powdered by agate mortar and pestle. The mixture was then put in a test tube and kept at 50 °C for 2 h. Decomposition of the reaction mixture with dilute HCl gave **4** in 95% yield (Table 1). Almost the same result was obtained when finely powdered **1** and **I** were mixed by shaking in a test tube for 5 min and then treated as above.

In both cases, particle size of the materials was 50-100 μ. Contrarily, heating of a solution of **1** (1 g) and **I** (3.8 g) in 50% aqueous MeOH (10 ml) under reflux for 2 h gave **4** in 60% yield. It is clear that the reaction in the solid state is more efficient than in solution. However, the reaction in the solid state proceeds very slowly at room temperature and is not accelerated by irradiation with ultrasound (Table 1). Nevertheless, it is surprising that one electron oxidation of **2** to **3** occurs more easily in the solid state than in solution. Water molecules of **I** would not be essential for the coupling reaction, because the irradiation with ultrasound of a mixture of finely powdered **1** and $[Fe(DMF)_3Cl_2][FeCl_4]$ (reagent **II**) at 50 °c in the solid state gave **4** in 79% yield (Table 1).

When a mixture of finely powdered **5** and two molar amounts of **II** was irradiated with ultrasound at 50 °C for 9 h in the solid state, **6** was obtained in 68% yield (Table 1). Contrarily, keeping a solution of **5** and two molar amounts of **II** in CH_2Cl_2 at room temperature for 48 h gave **6** in 33% yield in addition to byproducts such as 9-phenanthrone and 9,10-phenanthrenequinone. In this case, it is difficult to isolate **6** in a pure state. When a mixture of finely powdered **7** and two molar amounts of **I** was kept at 50 °C for 1 h in the solid state, **8** was obtained in 66% yield (Table 1). On the other hand, when the mixture was irradiated with ultrasound and shaken at 50 °C for 1 h, **8** was obtained in 89% and 84% yields, respectively (Table 1).

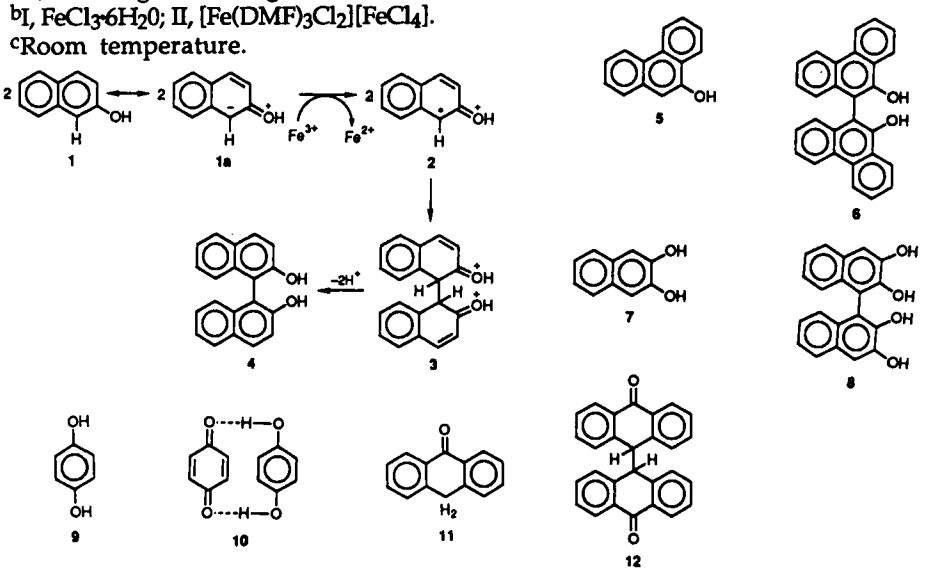
Irradiation with ultrasound of a mixture of finely powdered **9** and two molar amounts of **II** at 50 °C for 1 h gave **10** in 64% yield (Table 1). Not only phenols but also their keto forms gave coupling products by treatment with **I** in the solid state. Irradiation with ultrasound of a mixture of finely powdered **11** and two molar amounts of **II** at room temperature and 50 °C gave **12** in 82% and 97% yields, respectively (Table 1).

We also found that the coupling reaction proceeds in the presence of a catalytic amount of **I**. For example,

Table I. Oxidative Coupling Reactions in the Solid State

reactant	state[a]	reagent[b]	reaction conditions temperature,°C	time,h	product	yield,%
1	K	I	50	2	4	95
1	K	I	rt[c]	144	4	93
1	U	I	50	2	4	91
1	U	II	50	5	4	79
5	U	II	50	9	6	68
5	U	II	rt	9	6	0
5	K	II	50	9	6	20
7	K	I	50	1	8	66
7	U	I	50	1	8	89
7	S	I	50	1	8	84
9	U	II	50	1	10	64
11	U	I	rt	6	12	82
11	U	I	50	6	12	97
11	K	I	rt	12	12	0
11	K	I	50	6	12	77
11	S	I	rt	6	12	0

[a]K, standing; S, shaking; U, ultrasound (28 kHz).
[b]I, $FeCl_3 \cdot 6H_2O$; II, $[Fe(DMF)_3Cl_2][FeCl_4]$.
[c]Room temperature.



irradiation with ultrasound of a mixture of finely powdered 1 and a 0.2 molar amount of I at 50°C for 24 h gave 4 in 89% yield. This result shows that oxidation of Fe^{2+} to Fe^{3+} under air occurs easily in the solid state.