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Oxidative Coupling Reactions of Phenols with FeCl₃ in the Solid State

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OXIDATIVE COUPLING REACTIONS OF PHENOLS WITH FeC1 $_{
m 3}$ IN THE SOLID STATE

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ABSTRACT Some oxidative coupling reactions of phenols with FeCl₃ 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 FeCl₃.

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 FeCl₃ or manganese tris(acetylacetonate), although the latter — is too expensive to use in large quantities. The coupling reactions of phenols with FeCl₃, however, sometimes give quinones as byproducts. Recently, we found that the coupling reaction with FeCl₃ 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 FeCl₃.

EXPERMENTAL AND DISCUSSION

A mixture of 1 (1 g, 7 mmol) and FeCl₃·6H₂O (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 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 CH₂Cl₂ 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

reaction conditions						
reactant	statea	reagent ^b	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	7 9
5	U	II	50	9	6	68
5	U	П	rt	9	6	0
5	K	${f II}$	50	9	6	20
7	K	I	50	1	8	66
7	Ū	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	<i>7</i> 7
11	S	I	rt	6	12	0

irradiation with ultrasound of a mixture of finely powdered 1 and a 0.2 molar amount of I at $50\,^{\circ}\text{C}$ 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.