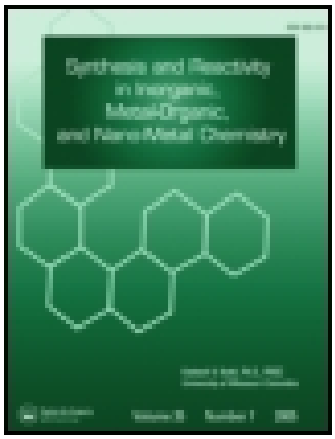

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Selective Oxidation of Benzoins with Chromic Acid Supported on Aluminum Silicate Under Viscous Conditions

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Selective Oxidation of Benzoins with Chromic Acid Supported on Aluminum Silicate Under Viscous Conditions

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Efficient oxidation of benzoins to corresponding benzils using chromic acid supported on aluminum silicate reagent under viscous conditions at room temperature is described, and all the reactions are completed within 3 hours in yields between 82–92%. The present procedure can overcome the problems existed in the common solvent-free reactions of the difficulty for the solid molecular collision to react. In addition, owing to the reaction using a very minimum amount of solvents, combustion, toxicity, and environmental pollution of the solvents are quite reduced.

Keywords Aluminum silicate, benzils, benzoins, chromic acid, oxidation, supported reagent

INTRODUCTION

Benzils are versatile compounds in organic chemistry that can be utilized for the preparation of a variety of molecules, many of which show a diversity of interesting biological activities.[1–6] It is well known that benzils can be obtained by the way of oxidation of benzoins with a wide range of reagents.

EXPERIMENTAL

Oxidation of Benzoin to Benzil; Typical Procedure

A mixture of benzoin (212 mg, 1 mmol) that is dissolved with a very minimum amount of dichloromethane (0.22 mL) to form a viscous liquid in advance and chromic acid supported on aluminum silicate reagent (750 mg) [28] in a normal test tube is shaken mechanically at room temperature for 3 h. The progress of the reaction is monitored by TLC using hexane:ethyl acetate (7:3) as eluent. The reaction mixture is then washed with dichloromethane (3 × 10 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane:ethyl acetate (7:3) to afford benzil (188 mg; 90%).

RESULTS AND DISCUSSION

The oxidative transformation of benzoins to benzils has been accomplished by a variety of chromium (VI) based reagents, for instance, chromyl chloride,[7] quinaldinium dichromate,[8] poly(2-vinyl-quinolinium) dichromate,[8] ammonium chlorochromate,[9,10,12,17,20] chromium oxide,[11] trimethylammonium chlorochromate,[13] pyridinium chlorochromate,[14] Jones reagent,[15] potassium dichromate,[16] quinoxalinium bromochromate,[18] pyridinium fluorochromate,[19] and piperdinium chlorochromate,[21] etc. The utility of chromium (VI) reagents in the oxidative transformation is compromised due to their inherent toxicity, cumbersome preparation and potential danger (possible ignition or explosion) in handling of its complexes, and difficulties in terms of product isolation and waste disposal. However, it seems that to use solid supported reagents under solvent-free conditions may circumvent some of these problems and may provide an attractive alternative in organic synthesis in view of the selectivity and associated ease of manipulation.[22,23] Unfortunately, under solvent-free conditions, it is, in general, not satisfied for solid substrates, like benzoins, performed at the room temperature because both of molecules, substrates and reagents, are in crystal forms that are of difficulty for collision to reach the reaction, so that such reactions are normally carried out at the temperature near or over the substrate melting point by either heating or other technologies in advance in order to dissolve the solid substrates into the liquid forms to increase the reaction rate.

More recently, we reported oxidation of benzoins to benzils with hexavalent chromium derivatives under different reaction conditions.[24–27] Even though the utility of chromium (VI) reagents in synthetic chemistry is compromised due to their inherent toxicity and potential danger as we mentioned above,

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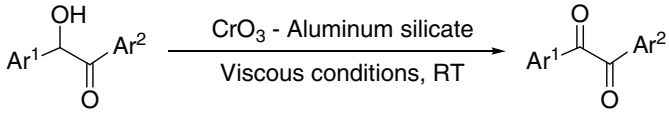
Ar^1	Ar^2
	
	
	
	
	

SCH 1.

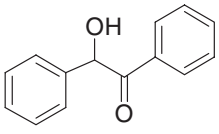
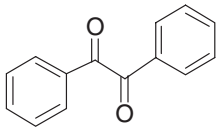
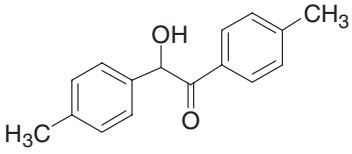
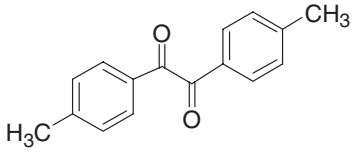
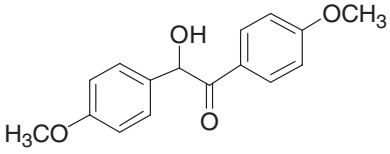
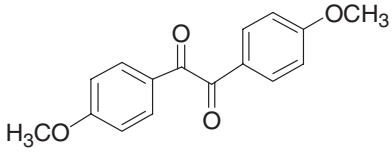
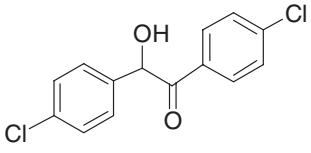
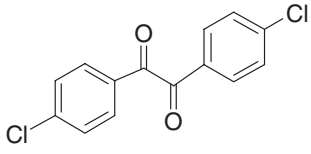
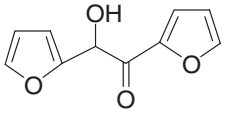
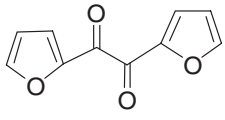
the researchers are continuously for the development of new chromium (VI) reagent for the effective and selective oxidation of organic substrates under mild condition. Therefore, to search for newer oxidizing agents is of interest to synthetic organic chemists.

As a part of our ongoing program related to developing new oxidation methods, and based on our previous investigations of both oxidation of alcohols with chromic acid supported on aluminum silicate reagent[28,29] and oxidation of solid benzoins with manganese dioxide under viscous conditions,[30] we wish to report here a simple and efficient procedure that can be used for the oxidative transformation of benzoins (**1**) into the corresponding benzils (**2**) using chromic acid supported on

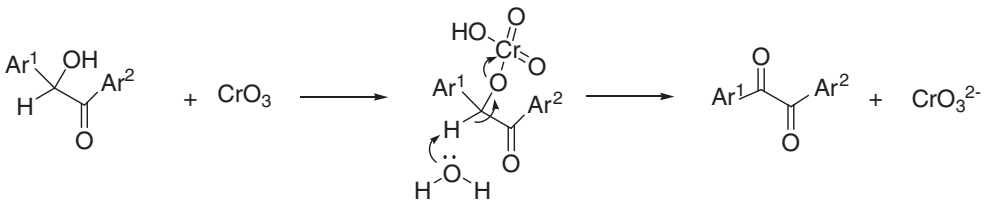


(1) **(2)**

TABLE 1
Oxidation of benzoins with chromic acid supported on aluminum silicate under viscous conditions

Substrate	Product[a]	Reaction time (h)	Yield[b](%)	m.p. (°C) Found	m.p. (°C) Reported[31]
		3	90	93–95	95
		3	92	101–103	104–105
		3	90	130–132	131–133
		3	82	197–198	197–199
		3	85	160–162	162

[a] All the products are known compounds and were identified by comparison of their spectra with the literature values.
[b] Yield of isolated pure product.



SCH 2.

aluminum silicate at room temperature under viscous conditions (Scheme 1), which can overcome the problems existed in the common solvent-free reactions of the difficulty for the solid molecular collision to react. The present procedure offers a simple and efficient oxidation method for the preparation of benzils, and is an extension of our previous work as well.

In the present study, a 1.5 to 1 molar ratio of chromic acid to substrate is employed.[28] First, the solid substrate is dissolved with a very minimum amount of dichloromethane to form a viscous liquid, and then the oxidant is added with care. The mixture is shaken magnetically at room temperature until TLC analysis indicates a completed reaction, and all the reactions are completed within 3 hours. Finally the residue is washed, and the product is then purified by preparative TLC. The results, which are shown in Table 1, show that this method is an efficient oxidation of solid benzoins, and gives the corresponding benzils in high yields. The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples.

The mechanism of the current oxidation that we consider is the same as the well-known one that is the oxidation of the secondary alcohols by chromium (VI) reagents, which involves the nucleophilic oxygen reacting with the chromium (VI) reagent to produce an intermediate, chromate ester (**3**), followed by decomposition of the ester to afford ketones (Scheme 2) described previously in the literature.[20,33]

The main advantages of the present procedure are that under viscous conditions, the oxidation of the solid substrates can be carried out very efficiently with mild process, and owing to the reaction, using a very minimum amount of solvents, combustion, toxicity, and environmental pollution of the solvents are quite reduced. Therefore it is, probably, over previous reported oxidation routes with chromium (VI)-based reagents as oxidants.

CONCLUSION

An efficient procedure for oxidation of benzoins to corresponding benzils using chromic acid supported on aluminum silicate reagent under viscous conditions at room temperature is described, which can overcome the problems existed in the common solvent-free reactions of the difficulty for the solid molecular collision to react and is an extension of our previous work as well.

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