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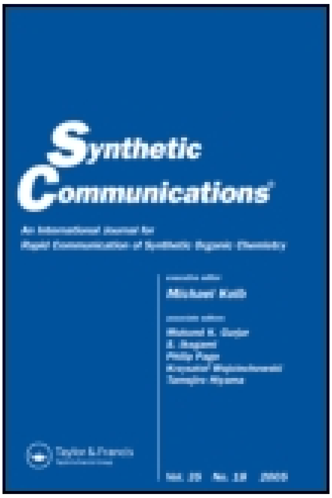


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# OXIDATION OF BENZOINS TO BENZILS WITH CHROMIUM TRIOXIDE UNDER VISCOUS CONDITIONS

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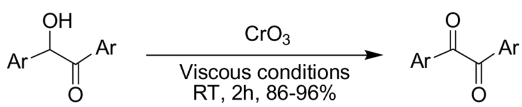
## GRAPHICAL ABSTRACT




(1) (2)

**Abstract** *An efficient and selective oxidation of benzoins into corresponding benzils using chromium trioxide under viscous conditions at room temperature is described. The present oxidations are completed within 2 h with the yield of 86–96%. It can overcome the problems of the common solvent-free reactions, in which it is difficult for the solid molecular collision to react.*

**Keywords** Benzils; benzoins; chromium trioxide; oxidation; viscous conditions

## INTRODUCTION

The oxidation of alcohols to the corresponding carbonyl compounds with hexavalent chromium derivatives is widely used in organic synthesis, and a large number of procedures have been described.[1–3] It is well known that carbonyl compounds in the chemical industry are precursors with wide applicability. However, the established chromium oxidation methods still have some disadvantages: mainly the chromium-based reagent must often be prepared. With methods involving use of aqueous acid and miscible organic solvents such as acetone[4] and dimethyl sulfoxide,[5] the solvent may be attacked by chromic acid, and sometimes thick reaction mixtures are produced, which hinder isolation of the product. Therefore, new experimental procedures for conducting oxidation with chromium reagents are still of interest, especially in the search of versatile and selective methods.

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## RESULTS AND DISCUSSION

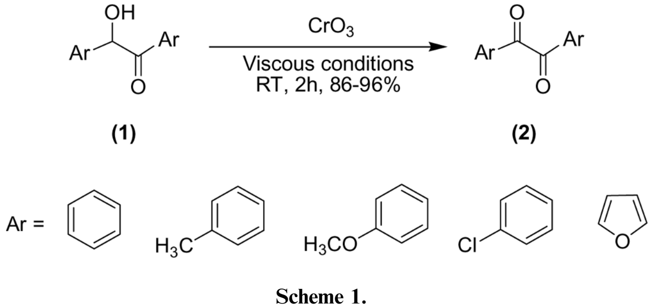
Benzils are synthetically important because of their wide practical applicability. They also find use as photosensitive agents in photocurable coatings and as interesting precursors for some pharmaceutically important compounds such as the antiepileptic phenytoin and the anticonvulsant dilantin.[6–11]

Mostly, benzils can be prepared by the way of oxidation of benzoins with chromium reagents. Up to now, several hexavalent chromium derivatives have been employed for this oxidation transformation, for instance, chromyl chloride,[12] quinaldinium dichromate,[13] poly(2-vinyl-quinolinium) dichromate,[13] ammonium chlorochromate,[14–18] chromium trioxide,[19–22] trimethylammonium chlorochromate,[23] pyridinium chlorochromate,[9] Jones reagent,[24] potassium dichromate,[25] quinoxalinium bromochromate,[26] pyridinium fluorochromate,[27,28] and piperdinium chlorochromate.[29] Although many diverse chromium methods are available for this oxidation, convenience, selectivity, and mild procedures are important objectives of current relevance.

Considerable attention has been paid to the solvent-free reactions in organic synthesis. Solvent-free reactions are not only of interest from ecological point of view, but in many cases also offer considerable synthetic advantages in terms of yield, selectivity, simplicity of the procedure, and operation at room temperature. These factors are especially important in industry. Unfortunately, under solvent-free conditions, these do not occur for solid substrates, such as benzoins, performed at room temperature because molecules, substrates, and reagents are in crystal forms, which make it difficult for the collision to reach the reaction, so such reactions are normally carried out at a temperature near or over the substrate melting point by either heating or other technologies. This dissolves the solid substrates into liquid forms, which increases the reaction rate. Therefore, some of the solvent-free reactions, especially for those solid substrates, may be modified to more modern and elegant versions.

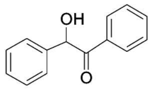
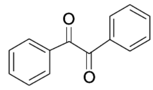
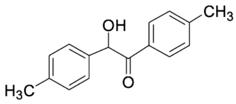
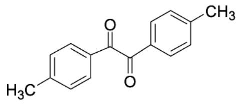
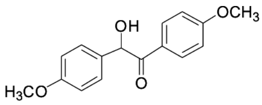
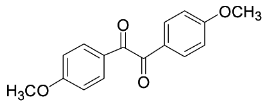
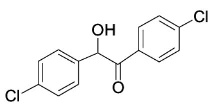
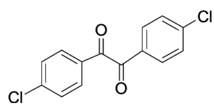
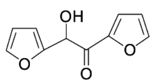
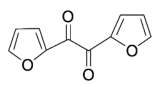
Previously, we described oxidation of alcohols with chromium trioxide under solvent-free conditions[30] and oxidation of solid benzoins with manganese dioxide under viscous conditions,[31] respectively. In continuation of these investigations, we report here a more efficient procedure for the oxidation of solid benzoins (**1**) into the corresponding benzils (**2**) using chromium trioxide under viscous conditions at room temperature (Scheme 1), which can overcome the problems in the common solvent-free reactions.

In the present procedure, a 1 to 2 molar ratio of the substrate to chromium trioxide is employed. The oxidation is very simple: first the solid substrate is




Scheme 1.

**Table 1.** Oxidation of benzoins with chromium trioxide under viscous conditions

| Substrate | Product[a] | Reaction time (h) | Yield[b] (%) | Mp (°C) Found | Mp (°C) Reported[32] |
|---|---|---|---|---|---|
|  |  | 2 | 96 | 93–95 | 95 |
|  |  | 2 | 92 | 103–104 | 104–105 |
|  |  | 2 | 86 | 130–132 | 131–133 |
|  |  | 2 | 93 | 194–196 | 197–199 |
|  |  | 2 | 89 | 159–161 | 162 |

[a]All the products are known compounds and were identified by comparison of their melting points with the literature values as well as by $^{1}$H NMR and IR.
[b]Yields of isolated pure products.

dissolved with a 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 thin-layer chromatographic (TLC) analysis indicates a completed reaction, and all the reactions are completed within 2 h. Finally the residue is washed, and the product is then purified by preparative TLC. The results in Table 1 show that this method efficiently oxidizes solid benzoins and gives the corresponding benzils in good yields. The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples.

The main advantages of the present procedure is that under viscous conditions the oxidation of the solid substrates can be carried out very efficiently using a shaking machine with mild process, and therefore it is clearly better than other previously reported chromium(VI)-based reagents. In addition, because the reaction uses a minimum amount of solvents, combustion, toxicity, and environmental pollution of the solvents are reduced. Likewise, compared with the oxidation using chromium trioxide–Kieselguhr under viscous conditions[21] that we reported before, the present procedure has no need of preparation for the supported reagent.

## EXPERIMENTAL

### Oxidation of Benzoin to Benzil: Typical Procedure

A mixture of benzoin (212 mg, 1 mmol) (dissolved with a minimum amount of dichloromethane (0.2 mL) to form a viscous liquid in advance) and chromium

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trioxide (200 mg, 2 mmol) in a normal test tube is shaken mechanically at room temperature for 2 h with care. The progress of the reaction is monitored by TLC (plates: aluminum-backed silica gel Merck 60 $GF_{254}$) using hexane–ethyl acetate (7:3) as eluent. The reaction mixture is then washed with dichloromethane ($3 \times 10$ mL). The combined filtrates are evaporated to give the crude product, which is purified by preparative TLC with hexane–ethyl acetate (7:3) to afford benzil (201 mg; 96%).

## CONCLUSION

In conclusion, an efficient procedure for oxidation of benzoins to corresponding benzils using chromium trioxide under viscous conditions at room temperature is described, which can overcome the problems in the common solvent-free reactions that make it difficult for the solid molecules to react.

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