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Solid State Oxidation of Benzoins on Alumina-Supported Copper(II) Sulfate under Microwave Irradiation†

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Benzoins are rapidly oxidised to benzils in high yields by the solid reagent system copper(II) sulfate–alumina, under the influence of microwaves.

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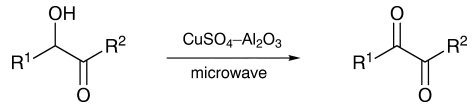
The oxidative transformation of benzoins to benzils has been accomplished by a variety of reagents namely nitric acid,[1] Fehling's solution,[1] thallium(III) nitrate (TTN),[2,3] ytterbium(III) nitrate,[4] clayfen[5] and ammonium chlorochromate–alumina.[6] Besides extended reaction times, most of these processes suffer from drawbacks such as the use of corrosive acids and toxic metallic compounds that generate undesirable waste materials. Consequently, there is a need for the development of a manipulatively easy and environmentally benign solvent-free protocol for the oxidation of benzoins. In this context, organic reactions on solid supports[7,8] and those assisted by microwaves,[8–10] especially under solvent-free conditions,[8,9] have attracted attention recently because of their enhanced selectivity, milder reaction conditions and associated ease of manipulation. Since only the polar reactants adsorbed on the surface of the solid support absorb microwaves, a variety of reagents supported on such surfaces can be utilised for the enhancement of organic reactions using an unmodified microwave oven.



We have an ongoing program to develop solvent-free synthetic protocols that are accelerated by ultrasound or microwave irradiation.[8] A recent report on the utility of copper salts for the oxidation of hydroquinones and coupling of naphthols[11] prompts us to report our results on the facile oxidation of benzoins to benzils that proceeds expeditiously using copper(II) sulfate impregnated on alumina. A wide variety of benzoins, symmetrical as well as unsymmetrical (Table 1), undergo rapid oxidation with this solid reagent system, $CuSO_4$–Al_2O_3, to afford vicinal diketones in high yields within 2–3 min of microwave irradiation. These solvent-free reactions are conducted by mixing benzoins thoroughly with the catalyst followed by irradiation in a domestic microwave oven. The optimum ratio of substrate to reagent is found to be (1:0.85, mole:mole) that ensures complete conversion of benzoins into benzils. Interestingly, the oxidative protocol is effective only for α-hydroxyketones; other secondary alcohols, including 1,2-diphenylethane-1,2-diol, are not oxidised under these conditions.

Experimental

Melting points are uncorrected. A Sears Kenmore household microwave oven operating at 2450 MHz was used at its full power of 900 W for all the experiments. The products were identified by comparison of the mp, IR and NMR spectra of the products with authentic samples.

Preparation of the Reagent, $CuSO_4$–Al_2O_3.—Neutral alumina (25 g) was added to a well stirred solution of copper sulfate pentahydrate (3.9 g) in distilled water (50 ml) vacuum. The resulting sky blue powder was stored in a tightly closed bottle and used without prior activation. The reagent retains its activity for an extended period; the original batch is still active 3 years after its preparation.

General Oxidation Procedure.—Benzoin (1 mmol) and $CuSO_4$–Al_2O_3 (1.5 g, 0.85 mmol of $CuSO_4 \cdot 5H_2O$) were mixed thoroughly on a vortex mixer. The reaction mixture contained in glass tubes was placed in an alumina bath (heat sink) inside the microwave oven and irradiated for a specified time. On completion of the reaction, followed by TLC examination (hexane-ethyl acetate, 9:1), the product was extracted into methylene chloride (3 × 10 ml). The solvent was removed under reduced pressure and the residue crystallised from an appropriate solvent to afford nearly quantitative yields of benzils.

That the effect may not be purely thermal[12] is borne out by the fact that for a similar product yield the reaction could be completed in 1.5 h (entry 1, Table 1) at the same bulk temperature of 120 °C using an alternate mode of heating (oil-bath); the temperature of the reaction mixture inside the alumina bath reached ~120 °C after 2 min of irradiation in a microwave oven operating at full power of 900 W.

In conclusion, this solvent-free oxidation of benzoins using $CuSO_4$-'doped' alumina is a simple and high-yielding protocol

Table 1 Oxidation of benzoins on $CuSO_4$–Al_2O_3 under microwave irradiation

Entry	R^1	R^2	*t*/min	Yield(%)[a]	mp (°C) found	mp (°C) reported
1	Ph	Ph	2.0	96	92–93	94–96[3]
2	Ph	*p*-MeC_6H_4	3.0	81	30–31	29–30[5]
3	Ph	*p*-$MeOC_6H_4$	2.5	85	62	62–63[5]
4	*p*-ClC_6H_4	*p*-ClC_6H_4	3.5	82	194–196	195–197[3]
5	*p*-MeC_6H_4	*p*-MeC_6H_4	2.0	92	102–104	101–104[3]
6	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	2.5	86	131–133	132–134[3]
7			2.5	82	161–163	162–164[6]

[a]Refers to pure isolated products obtained.

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which avoids the drastic conditions that are typical of conventional oxidation reactions. Yet another environmentally benign feature is that the alumina support employed can be recovered and reused after washing off the products; the usual activation of the support by heating at elevated temperatures under vacuum for extended periods is not required.

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