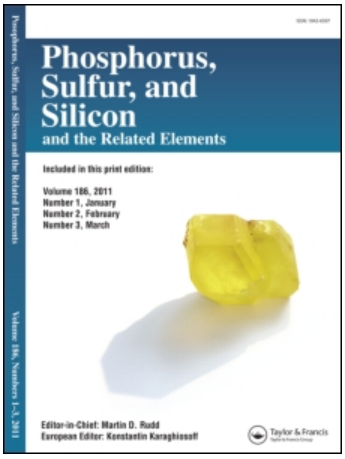

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SILICA GEL SUPPORTED $Bi(NO_3)_3$, $5H_2O$; AN EFFICIENT REAGENT FOR OXIDATION OF BENZOINS UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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Benzoines are oxidized to benzils using $Bi(NO_3)_3$, $5H_2O$ as oxidant in a solventless system under microwave irradiation.

Keywords: benzoines; $Bi(NO_3)_3$, $5H_2O$; solventless system

Oxidation of benzoines is one of the important routes of preparation of benziles. Benziles have received a great deal of attention because of their practical applications, i.e., as photosensitive agents and as synthetic agants in organic and pharmaceutical chemistry. Oxidation of benzoine derivatives with an oxidizing agent is a common method for the preparation of benziles. It has been reported that benzoines can be oxidized to benziles by nitrosonitric acid, $CuSO_4$/Py, $[Fe(CN)_6]^{3-}/OH^-$ and Bi_2O_3/H^+ in water[1–5] or by Ph_3PBr_2/MeCN,[6] DMSO/$(COCl_2)_2/CH_2Cl_2$,[7] $PhCH_2N^+EtBr$/MeCN,[8] NBS/CCl,[9] Clayfen/n-C_6H_{14},[10] Bu_2SnO and $Bu_2Sn(OMe)_2$,[11] Tr(Opr-I),[12] and $(CH_3)_2NHCrO_3Cl/SiO_2$[13] in an organic solvent, but long reaction periods, use of toxic metallic compounds and corrosive acids, tedious purification and undesirable side products are some disadvantages of these methods. Consequently, easy, rapid, convenient, and environmentally benign protocols for the oxidation of benzoines are required. In the last few years there has been an interest in the use of microwave heating in organic synthesis. The use of such nonconventional reaction conditions reveals features like a short reaction time compared to conventional heating, ease of work-up after reaction, and reduction in usual thermal degradation and better selectivity. Therefore microwave-assisted reactions for oxidation of benzoines are[14,15] popular. Hydrated

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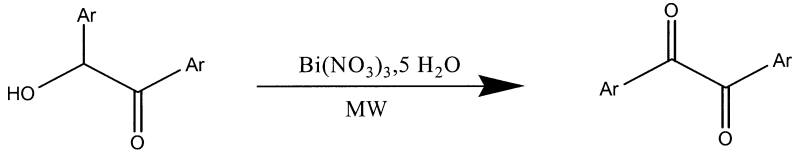
Bismuth(III)nitrate, $Bi(NO_3)_3$, $5H_2O$, is an excellent oxidant and has also been used as dehydrogenating agent.[16] In this article, we report a new method of the preparation of benziles under solvent-free condition with $Bi(NO_3)_3$, $5H_2O$ as the oxidant (Scheme 1). A series of benzoines undergo rapid oxidation with $Bi(NO_3)_3$, $5H_2O$ to afford vicinal diketones, showing that $Bi(NO_3)_3$, $5H_2O$ is a convenient and useful oxidant for oxidation of benzoines to benziles. The benziles that were prepared are listed in Table I.



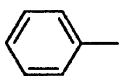
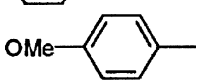
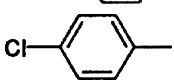
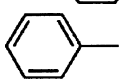
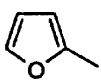
1 **2**

SCHEME 1

EXPERIMENTAL

Melting points were measured with an electro thermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Philips PU 9800

TABLE I Prepared Benziles by the Oxidation of Benzoines with $Bi(NO_3)_3$, $5H_2O$ as the Oxidant

			m.p./°C	
Ar	Reaction time (min)	Yields (%)	Found	Reported
	1	95	93–94	95[17]
	1.5	92	130–133	132–134[18]
	1	94	194–196	195–197[18]
	1	92	160–162	162–164[19]
	0.5	95	100–103	101–104[18]

FT IR instrument. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-90A spectrometer at 90 and 22.6 MHz. All products are known compounds; their physical and spectroscopic data were compared with those of authentic samples and were found to be identical.

GENERAL PROCEDURE

One gram silica gel was added to the solution of 1 mmol of an appropriate benzoine (**1**) and 0.4 g $Bi(NO_3)_3$, $5H_2O$ in CH_2Cl_2 (5 ml) at room temperature. The reaction mixture was thoroughly mixed, and the adsorbed material was dried and placed in the microwave oven operating at medium to high power for the time indicated (Table I). Then the resulting crude product was extracted with 3×20 cm^3 of CH_2Cl_2. The solvent was evaporated. The residue was recrystallized from ethanol to give pure benziles (**2**).

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