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Microwave-assisted efficient synthesis of diimines in dry media using silica gel supported sodium hydrogen sulfate as reusable solid support

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A simple and efficient method for synthesis of diimines using silica gel supported sodium hydrogen sulfate as reusable solid support in solvent-free conditions under microwave irradiation is described.

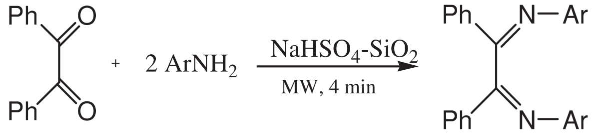
Keywords: benzil diimine, $NaHSO_4$–SiO_2, solvent-free conditions

Diimines are synthetically useful as precursor for a variety of biologically important heterocycles[1] and also as chelating compounds.[2] Accordingly, substantial attention has been paid to developing efficient methods for the synthesis of diimine derivatives.[3]

During the past few years, a number of publications and reviews have advocated the use of microwave technology in organic synthesis.[4] The combination of solvent-free reaction conditions and microwave irradiation leads to large reduction in reaction times, enhancements in conversions, and sometimes in selectivity with several advantages of the eco-friendly approach, termed green chemistry.[5]

Recently, the use of surface active catalysts and inorganic reagents has received much attention because of their enhanced selectivity, milder conditions, simple workup, ease of handling and recyclability of catalysts.[6] Particularly, silica gel supported sodium hydrogen sulfate ($NaHSO_4$–SiO_2) has advantages of low cost, ease of preparation, and catalyst recycling.[7]

In continuation of our interest on microwave-assisted organic transformations,[8] herein we report a simple, convenient and efficient method for the preparation of benzil diimine derivatives under solvent-free conditions using microwave irradiation in the presence of $NaHSO_4$–SiO_2 as an inexpensive, eco-friendly and recyclable solid support (Scheme 1).



1 **2** **3**

Scheme 1

As can be seen from results reported in Table 1, a mixture of benzil **1** and aromatic amines **2** on a $NaHSO_4$–SiO_2 surface are converted to the corresponding benzil diimines **3a–d** in solvent-free conditions using microwave irradiation in good yields. The synthesis of benzyl diimines have been reported using Al_2O_3 as catalyst under MW irradiation.[3h] When compared to Al_2O_3 catalyst (Table 1), the yields of benzyl diimines in the presence of $NaHSO_4$–SiO_2 are slightly higher.

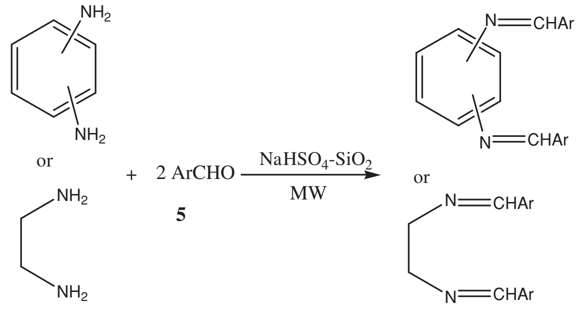
Table 1 Microwave-assisted synthesis of benzil diimines

Entry	Ar	Yields/%[a]		Melting point/°C	
3		A[b]	B[c]	Found	Reported
a	C_6H_5	72,71,70[d]	62	142–144	140[e]
b	4-MeC_6H_4	75	69	152–153	154[e]
c	4-$MeOC_6H_4$	79	72	159–161	159[e]
d	4-ClC_6H_4	65	58	164–166	165[e]

[a]Isolated yields; [b]method A: new reaction conditions (cat. $NaHSO_4$-SiO_2); [c]method B: Singh conditions (cat. Al_2O_3)[3h]. [d]The same solid support was used for each of the three runs. [e]Ref. 3h.

The condensation of benzil **1** and aniline was also performed in the absence of $NaHSO_4$–SiO_2 under neat conditions and microwave irradiation; however, the yield of **3a** was low (22%). Entry **3a** describes the yields of three consecutive condensations leading to 1,2,3,4-tetraphenyl-1,4-diaza-1,3-butadiene. In these experiments the product was extracted with ethyl acetate and solid residue washed with EtOAc and dried at 100 °C for 3h; the system can be reloaded with fresh reagents for further runs. Thus, recyclisation of solid support is possible without significant loss of activity (Table 1).

In order to study the generality of this new methodology, we carried out reaction of a variety of diamines **4** with aromatic aldehydes **5** which also afforded the diimines **6** in high yields (Scheme 2).



4 **6**

Scheme 2

Diamine	Ar	Yields/%[a]/	Melting point/°C	
4		Time/min	Found	Reported
$NH_2(CH_2)_2NH_2$	C_6H_5	82/2	51–53	52–53[b]
$NH_2(CH_2)_2NH_2$	4-$MeOC_6H_4$	85/2	109–112	109–110[b]
$NH_2(CH_2)_2NH_2$	C_6H_5-C=C-	89/2	106–107	108–109[b]
1,2-$(NH_2)_2C_6H_4$	C_6H_5	68/4	134–137	135[c]
1,4-$(NH_2)_2C_6H_4$	C_6H_5	78/4	136–138	139[c]
1,3-$(NH_2)_2C_6H_4$	C_6H_5	75/4	108–110	109[c]

[a]Isolated yields, [b]ref. 1c,[c] ref. 3a.

In conclusion, a simple, efficient, high yielding and green protocol for the synthesis of diimine derivatives using silica gel supported sodium hydrogen sulfate as solid support in solvent-free conditions under microwave irradiation has been reported.

Experimental

Melting points were measured on an Electro thermal 9100 apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-470 Spectrophotometer. ^1H NMR and ^{13}C NMR spectra were determined on Bruker 500 DRX AVNCE instrument at 500 and 125 MHz, respectively. The microwave oven was a domestic (max. 900 w) National model NN-6653 with select power levels. All the

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products are known compounds and were characterised by IR and ^{1}H NMR spectroscopic data, and their melting points were compared with reported literature values.

Synthesis of 1,2,3,4-tetraphenyl-1,4-diaza-1,3-butadiene; typical procedure: A mixture of benzil **1** (1 mmol, 0.21 g), aniline (2.5 mmol, 0.23 g) and $NaHSO_4$–SiO_2 (0.50 g, prepared by reported method[7b]) were finely mixed together. The reaction mixture was placed in a beaker and irradiated for 4 min in a domestic microwave oven at 900 W.After cooling, the reaction mixture was extracted with EtOAc (2 × 10 ml) and the solvent removed on a rotary evaporator. The residue was charged directly on a small silica gel column (60–120 mesh), and eluted with ethyl acetate–hexane (3:7) to afford pure product **3a** (0.26 g, 72%); m.p. 142–144 °C, IR (KBr) (ν_{max}, cm^{-1}): 1619 (C=N); ^{1}H NMR ($CDCl_3$, Me_4Si): δ_H 6.81–7.86 (20 H, m, arom.); ^{13}C NMR ($CDCl_3$, Me_4Si): δc 121.10, 124.38, 128.70, 128.85, 129.30, 130.92, 138.20, 149.75, 165.03.

Synthesis of N,N'-Ethylenebis[benzylidenealdimine]; typical procedure: Ethylenediamine (1 mmol), benzaldehyde (2.5 mmol, 0.27 g) and $NaHSO_4$–SiO_2 (0.50 g) were finely mixed together. Then mixture was placed in a beaker and irradiated for 2 min in a domestic microwave oven at 900 W. After cooling, the reaction mixture was treated with a solution of EtOAc–hexane (1:5) and filtrated to give pure product (0.19 g, 82%); m.p. 51–53 °C, IR (KBr) (ν_{max}, cm^{-1}): 1612 (C=N); ^{1}H NMR ($CDCl_3$, Me_4Si): δ_H 3.90 (4H, s, 2CH_2), 7.1–7.9 (10 H, m, arom.), 8.3 (2H, s, CH); ^{13}C NMR($CDCl_3$, Me_4Si): δc 61.10,127.90, 128.21, 130.11, 135. 93, 162.30.

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