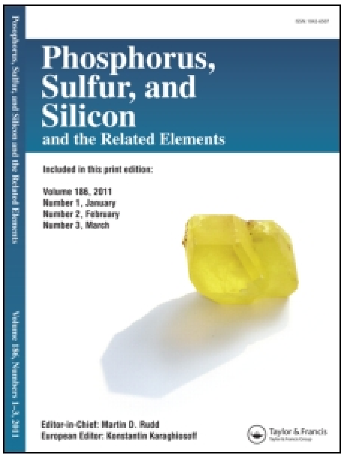

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Preparation of *N*-Arylsulfonyl Imines from Sulfonamides and Aryl Aldehydes Using Magnesium Oxide as a Heterogeneous and Reusable Catalyst Under Solvent-Free Conditions

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Preparation of *N*-Arylsulfonyl Imines from Sulfonamides and Aryl Aldehydes Using Magnesium Oxide as a Heterogeneous and Reusable Catalyst Under Solvent-Free Conditions

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An efficient solvent-free procedure for the preparation of N-arylsulfonyl imines from sulfonamides and aryl aldehydes in the presence of a catalytic amount of magnesium oxide and tetrabutylammonium bromide (TBAB) under microwave irradiation is described. The advantages of this method are good to high yields, short reaction times, low cost, and matching with green chemistry protocols.

Keywords Aldehyde; magnesium oxide; microwave; *N*-arylsulfonyl imine; solvent-free; sulfonamide

INTRODUCTION

N-Sulfonyl imines are versatile intermediates in organic synthesis.[1] They are excellent substrates in aza Diels-Alder reactions,[2] nucleophilic additions[3] and reductions,[4] as well as in radical[5] or ene reactions.[6] They have been also used in the synthesis of aziridines.[7] Several synthetic methods for the preparation of *N*-sulfonyl imines have been reported so far.[8–21] Most of them involve the condensation of sulfonamides

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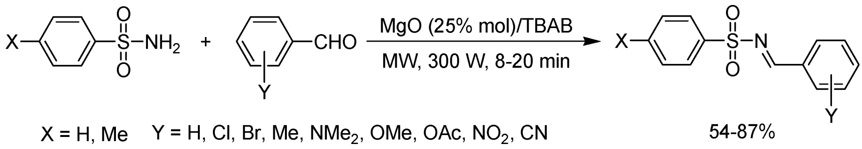
with aldehydes in the presence of strong Lewis acids. In many cases, strongly acidic conditions are not compatible with other functionalities present in a given substrate. Some methods need two-steps procedures or they are expensive methods and generate toxic byproducts. Moreover, some methods require the preparation of the starting materials such as oxime, sulfinylimine and/or aziridine.[13,14,17] Because of the limitations of the above methods, development of a new method for the synthesis of *N*-sulfonyl imines under basic conditions in one step would be desirable.

Recently, mineral oxides have proved to be useful to chemists in the laboratory as well as in industry due to the effective activation of adsorbed compounds and the enhancement of reaction rate, selectivity, easier workup, recyclability of the supports and the eco-friendly reaction conditions.[22] Magnesium oxide is one of these oxides: it is inexpensive, reusable, commercially available and an environmentally benign catalyst. Magnesium oxide has been extensively studied as a promising catalyst,[23] modifier, or promoter,[24] and catalyst support in several transformations such as Michael addition and Knoevenagel condensation,[25] transformation of ethanol to butanol[26] and self-condensation of propanol.[27]

Solvent-free organic reactions have been applied as a useful protocol in organic synthesis. Solvent-free reactions under thermal or microwave conditions often lead to shorter reaction times, increased yields, and easier workup. They match with green chemistry protocols and may enhance the regio- and stereoselectivity of reactions.[28]

Considering the above aspects, and along with our previous work on the synthesis of *N*-sulfonyl imines published in this journal,[9] as well as in extension of our previous studies on solvent-free organic syntheses,[22a,29] we report here a clean, facile and rapid method for the preparation of *N*-arylsulfonyl imines from sulfonamides and aryl aldehydes in the presence of a catalytic amount of magnesium oxide and tetrabutylammonium bromide (TBAB) under microwave irradiation (Scheme 1).



SCHEME 1

TABLE I The Influence of Various Basic Catalysts on the Reaction of Benzenesulfonamide with Benzaldehyde in the Presence of TBAB Under Microwave Irradiation (300 W, max. 110°C)

Catalyst	Time (min)	Yield[a] (%)
MgO	8	87
CaO	8	74
Cs_2CO_3	8	61
K_2CO_3	8	68
t-BuOK	8	53
DABCO	12	65
NBu_3	12	57
1-Methyl-imidazole	12	60

[a] Isolated yield.

RESULTS AND DISCUSSION

To determine the optimal reaction conditions we have studied the reaction of benzenesulfonamide with benzaldehyde as a model reaction to provide compound **1** (Scheme 1 and Table I). At first, the effect of various basic catalysts was examined to evaluate their capabilities. The results are summarized in Table I. As shown in Table I higher yields and shorter reaction times were achieved when MgO was used. Therefore, MgO was chosen as catalyst for all the other reactions.

In order to select the appropriate microwave power the model reaction was examined at different microwave powers (100–600 W) with controlled temperature (max. 110°C) in the presence of MgO and TBAB. The best results were observed at 300 W of microwave power.

In another study, the role of TBAB was evaluated. The absence of TBAB in the reaction medium afforded low yields even when the reaction time or the microwave power was increased. Thus, the presence of TBAB in the reaction mixture is critically significant. TBAB absorbs the microwave irradiation, generates in situ heat and increases the temperature above its melting point (100–103°C). In addition TBAB creates a homogeneous medium similar to that of an ionic liquid.[28a]

To investigate the versatility, as well as the capacity of our method, the reaction of sulfonamides with various structurally diverse aromatic aldehydes were examined (Table II). As indicated in Table II, the reactions proceeded efficiently and the *N*-arylsulfonyl imines were obtained in good to high yields in short reaction times.

It has been observed that the electronic properties of the aromatic ring of aldehydes affected the reaction. The results showed that halogen

TABLE II Preparation of *N*-Arylsulfonyl Imines from Sulfonamides and Aldehydes in the Presence of Catalytic Amounts of MgO and TBAB Under Microwave Irradiation (300 W, max. 110°C)

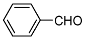
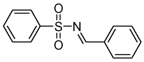
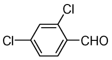
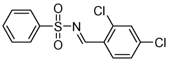
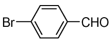
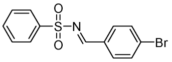
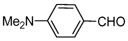
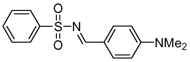
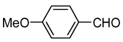
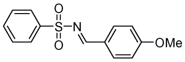
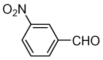
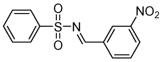
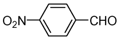
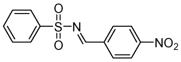
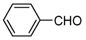
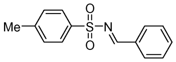
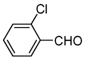
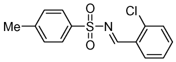
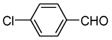
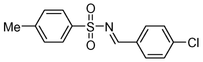
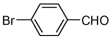
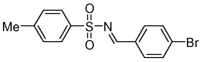
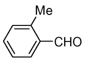
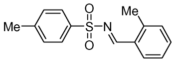
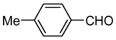
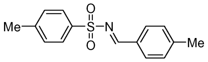
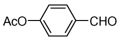
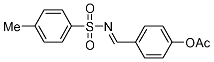
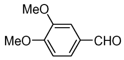
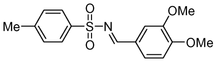
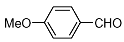
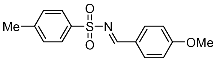
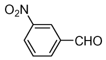
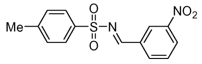
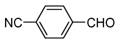
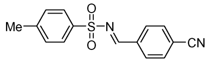
Aldehyde	Product	M. p. (Lit.)	Time (min)	Yield[a] (%)
		77–80 (78–81)[18]	8	87
		123–124 (125–126)[8]	15	64
		205–207 (208–209)[19]	12	85
		206–207 (209–210)[11]	15	79
		130–132 (131–132)[20]	12	84
		113–114 (111)[11]	15	62
		164–165 (162–164)[21]	15	56
		108–109 (109)[16]	12	80
		126–128 (126–128)[9]	20	60
		172–173 (172–173)[8]	15	77
		181–183 (182–185)[18]	15	78
		88–90 (91–92)[16]	20	54
		112–114 (111–112)[8]	15	76
		118–120 (121–123)[18]	15	75

TABLE II Preparation of *N*-Arylsulfonyl Imines from Sulfonamides and Aldehydes in the Presence of Catalytic Amounts of MgO and TBAB Under Microwave Irradiation (300 W, max. 110°C) *(Continued)*

Aldehyde	Product	M. p. (Lit.)	Time (min)	Yield[a] (%)
		111–114 (114–117)[18]	17	71
		126–128 (128–129)[8]	15	73
		102–104 (101–102)[8]	20	57
		172–173 (172–173)[9]	20	59

[a] Isolated yield.

atoms as well as electron-donating substituents had no significant effect on the yields (Table II). However, aryl aldehydes possessing electron-withdrawing or sterically demanding substituents generally need longer reaction times, and the yields are lower (Table II). It should be mentioned that the yield of *N*-arylsulfonyl imines resulting from the reaction of benzenesulfonamide with aldehydes was higher than that starting from 4-methyl benzenesulfonamide.

The interesting behavior of magnesium oxide lies in the fact that it can be reused after simple washing with ethyl acetate, thus rendering the process more economic. The yields of compound **1** (model compound) when MgO was used for the 2nd, 3rd, 4th, and 5th time were almost as high as when it was used for the first time.

In conclusion, the procedure presented here provides a clean, rapid and efficient solvent-free route to *N*-arylsulfonyl imines *via* the reaction of sulfonamides with aryl aldehydes using cheap and safe reagents.

EXPERIMENTAL

All chemicals were obtained from Merck or Fluka. The compounds were identified by the comparison of their melting points and/or ^{1}H and ^{13}C NMR data with those of authentic samples. All reactions were carried out using a CEM MARS 5^{TM} microwave oven. The ^{1}H (250 MHz) and ^{13}C (62.5 MHz) NMR spectra were obtained with a Bruker Avance DPX-250 spectrometer. Melting points were recorded with a Büchi B-545 apparatus in open capillary tubes and are uncorrected.

General Procedure for the Preparation of *N*-Arylsulfonyl Imines from Sulfonamides and Aryl Aldehydes Under Solvent-Free Conditions

To a well ground mixture of the sulfonamide (2 mmol), MgO (0.020 g, 0.5 mmol) and TBAB (0.129 g, 0.4 mmol) in a microwave vessel was added the respective aldehyde (2.6 mmol),[30] and the compounds were carefully mixed with a tiny spatula. The mixture was irradiated in the microwave oven at 300 W for the times reported in Table II. The microwave oven was programmed to give a maximum internal temperature to 110°C. The reaction mixture was cooled to room temperature, suspended in ethyl acetate (50 mL), filtered, and the filtrate was washed with water (2 × 50 mL) and dried over $MgSO_4$. The filtrate was concentrated to 5 mL, *n*-hexane (20–30 mL) was added, and the solution was allowed to stand at room temperature for 5–6 h. During this time crystals formed, which were collected by filtration, washed with *n*-hexane (20 mL) and dried.

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