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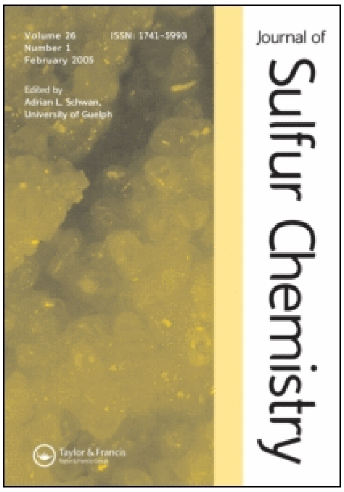

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Microwave-assisted β-elimination of sulfoxides on KF/Al_2O_3 support under solvent-free conditions

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Microwave-assisted *β*-elimination of sulfoxides on KF/Al_2O_3 support under solvent-free conditions

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(Received 11 July 2005; in final form 15 October 2005)

A fast, efficient and environmentally benign solvent-free procedure has been developed for microwave-assisted β-elimination of sulfoxides on KF/Al_2O_3 support. Various compounds such as olefins, ketones, α, β-unsaturated carbonyl compounds and β-ketoesters were prepared using this protocol. The reactions are very fast and clean. The products are produced in good to excellent yields relatively in short times. The support can be recycled for subsequent reactions without any appreciable loss of efficiency.

Keywords: Microwave; Sulfoxide; β-elimination; KF/Al_2O_3; Solvent-free

1. Introduction

In recent years, solvent-free reactions using either organic or inorganic solid supports have received increasing attention [1]. There are several advantages to performing reactions in dry media: a) short reaction times, b) increased safety, c) economic advantages due to the absence of solvent. KF/Al_2O_3 support is effective because the end products can easily be separated. Moreover KF/Al_2O_3 can function as a convenient medium and also act as a basic catalyst [2].

The utilization of microwave irradiation in organic synthesis is becoming increasingly popular [3, 4]. In many cases product purity and reaction times are improved when compared to conventional methods, with improvements often being attributed to reduction in latent heating times, superheating of solvents and more recently, implementation of microwave specific effects [5, 6]. In addition, solvent-free microwave irradiation processes are also clean and efficient.

The sulfinyl group has received attention in organic synthesis [7–10], by virtue of its ability to stabilize carbanions and to function as an alkene precursor. On heating sulfoxides with hydrogen in the β-position and which readily can adopt a syn conformation, a sulfenic acid is eliminated with introduction of a double bond. The reaction could proceed either by base catalysed or by simple pyrolysis (scheme 1). The method has been used for the preparation of α, β-unsaturated esters, acids, ketones and other conjugated alkenes. A literature survey indicates

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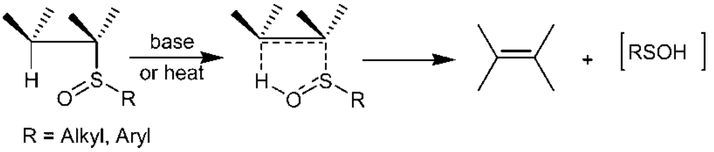
that various solvents such as benzene, toluene, dioxane and pyridine have been employed for this elimination. The required temperature is usually 80–160 °C and the process takes several hours to complete. Recently, we have reported the rapid β-elimination of sulfoxides either in solvent and/or in solvent-free conditions under microwave assisted irradiation. The use of microwave irradiation accelerated the reactions providing products in a very short time [11, 12].



SCHEME 1

We report here an efficient β-elimination of sulfoxides in the presence of KF/Al_2O_3 support. We found that various alkyl and aryl sulfoxide compounds easily converted to adducts in quantitative yields. In a typical procedure, irradiation of 2-benzenesulfinyl-1-phenylethanol as a model compound gave 96% yield of acetophenone (see experimental part). The results are summarized in table 1. This method has been used for the preparation of olefins (table 1, entries 1, 2, 8, 11, 12, 13), ketones (table 1, entries 3, 4, 5, 6), α, β-unsaturated carbonyl compounds (table 1, entries 7, 9) and β-ketoesters (table 1, entries 10). The reaction is simple, fast, clean and the yields are excellent. The comparison of our results with those reported using the conventional methods [11] under basic conditions (for example: potassium tertbutoxide, 55 °C, 17 hrs, 90% yield for diisopropyl sulfoxide) reveals the advantage of our solid support

Table 1. Microwave-assisted β-elimination of sulfoxides on KF/Al_2O_3 support.

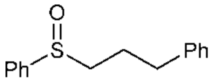
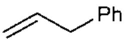
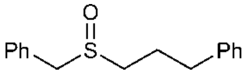
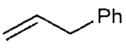
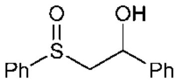
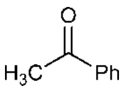
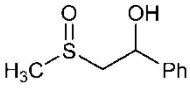
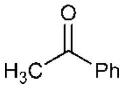
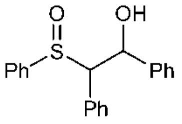
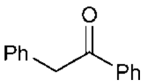
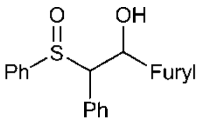
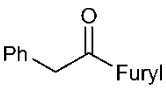
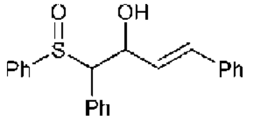
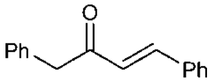
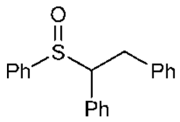
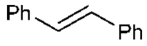
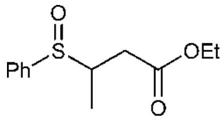
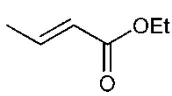
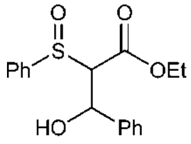
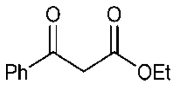
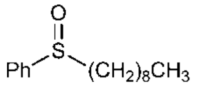
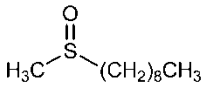
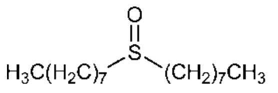
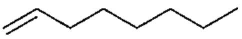
Entry	Sulfoxides	Products	Yield(%)^a
1	 **(1a)**		94
2	 **(1b)**		91
3	 **(2a)**		96
4	 **(2b)**		92
5	 **(2c)**		90
6	 **(2d)**		91

Table 1. Continued.

Entry	Sulfoxides	Products	Yield(%)[a]
7	 **(2e)**		95
8	 **(4a)**		92
9	 **(4b)**		93
10	 **(3a)**		94
11	 **(1c)**		95
12	 **(1d)**		96
13	 **(1e)**		95

[a] All yields refer to isolated products and all products were characterized by m. p., IR, ^{1}H-NMR, and their physical data were similar to those reported in the literature [11].

basic conditions and microwave irradiation. Also this support is non-volatile, non-flammable, eco-friendly, clean, safe, recyclable and easily prepared.

In conclusion KF/Al_2O_3 support has been shown to be an efficient catalyst for dehydro sulfinylation of alkyl or aryl sulfoxides under solvent-free conditions using microwave irradiation.

2. Experimental

The compounds gave satisfactory all spectroscopic data. IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids on a Nicolet spectrometer (Magna 550). A Bruker (FT-80 AC) NMR was used to record the ^{1}H NMR spectra. All NMR spectra were determined in $CDCl_3$ at ambient temperature. Melting points were determined on a Buchi B540 apparatus. The microwave oven used for this work was a National (1550 W) at 2450 MHz (100% power for all reactions). The sulfoxides studied were all either racemic or mixtures of diastereoisomers. Sulfoxides **1a–e** were prepared by oxidation of the appropriate sulfides with sodium metaperiodate in aqueous methanol [13]. Sulfoxide **2a–e** were prepared by condensation of the α-sulfinylcarbanions to the appropriate aldehydes [14]. Compound **3a** was synthesized by known method [15]. All other compounds were known and gave satisfactory spectroscopic data in agreement with literature.

2.1 *Selected spectroscopic data*

2a: mp 122.8 °C; ^{1}H NMR δ 7.21–7.82 (m, 10H, Ar), 5.35 (2xt, 1H), 5.1 (d, 1H, OH), 3.12–3.0 (dq, J 16 Hz, 17.6 Hz); IR 3250, 3080, 2880, 2850, 1490, 1440, 1070, 1020 (SO), 990 cm^{-1}.
2b: mp 98 °C; ^{1}H NMR δ 7.4 (m, 5H), 5.47 (m, 1H), 4.5 (br, 1H), 3.1 (m, 2H), 2.65 (s, 3H); IR 3238, 3046, 1600, 1430, 1046 (SO), 755 cm^{-1}.
2c: mp 167.6 °C; ^{1}H NMR δ 6.72–7.41 (m, 15H, 3 Ar), 5.62 (m, 1H), 3.52–4.1 (m, 2H); IR 3248, 1453, 1023(SO), 752 cm^{-1}.
2d: mp 122.5 °C; ^{1}H NMR δ 6.52–7.50 (m, 13H), 6.11 (br, 1H), 5.6 (d, 1H), 4.1 (m,1H); IR 3410, 3052, 1489, 1048 (SO), 757 cm^{-1}.
2e: mp 111.5 °C; ^{1}H NMR δ 6.9–7.41 (m, 15H, Ar), 6.32–6.80 (m, 1H), 5.75–6.22 (m, 1H), 5–5.35 (m, 1H), 3.41–3.9 (m, 1H); IR 3276, 3053, 2923, 1500, 1453, 1107, 1030 (SO), 976 cm^{-1}.
3a: mp 126.5 °C, ^{1}H NMR δ 7.24–7.7 (m, 10H, Ar), 5.25 (bt, 1H), 3.6–4.2 (m, 3H), 3.52 (d, 1H, OH), 0.9 (t, 3H); IR 3430, 3061, 2984, 2932, 1730 (CO), 1092, 1046 (SO), 738 cm^{-1}.
Product of **(2d):** ^{1}H NMR δ 7.12–7.45 (m, 7H), 6.35 (m, 1H), 3.95 (s, 2H); IR 3030, 1694, 1600, 1452, 1235, 751 cm^{-1}.
Product of **(2e):** ^{1}H NMR δ 7.6 (d, J 14.5 Hz, 1H), 7.25–7.46 (m, 10H), 6.72 (d, J 14.7 Hz, 1H), 3.84 (s, 2H); IR 3061, 2900, 1700, 1607, 1453, 757 cm^{-1}.

3. Procedure for the preparation of KF/Al$_2$O$_3$ support

The KF/Al$_2$O$_3$ support was prepared according to previously reported procedure with some modifications [16]. A mixture of potassium fluoride (45 g) and basic alumina (55 g, type T, Merck) in water (100 mL) was stirred at room temperature for 10 minutes. The resulting suspension was concentrated in vacuo and dried in a vacuum oven at 120 °C for 15 h. Use of basic alumina in the solid support gave the best results.

4. General procedure for microwave irradiation of sulfoxides

To a solution of 0.01 mol sulfoxide in dichloromethane (5 ml) was added 0.6 g KF/Al$_2$O$_3$ support. After evaporation of solvent under vacuum, the solid residue was placed in a Teflon flask (~20 ml) and subjected to microwave irradiation for four minutes. The reaction mixture was extracted with dichloromethane and was purified by column chromatography on silica gel or PTLC.

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