

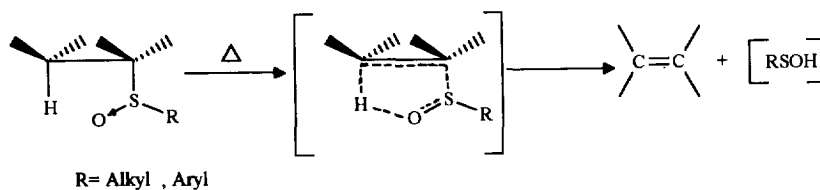
Rapid Dehydrosulfenylation of Sulfoxides Under Microwave Irradiation

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Abstract: Pyrolytic β -elimination of sulfoxides has been promoted by microwave irradiation. The reaction is very fast and yields are almost quantitative.

The rich chemistry of sulfoxides make them very useful reagents in organic synthesis^{1a-d}. One of the important reaction of sulfoxides is the pyrolytic β -elimination of sulfenic acids from sulfoxides². There are two convenient methods for this conversion; base catalysed β -elimination³ and simple pyrolysis. Both of these reactions convert the sulfoxides to unsaturated compounds. The geometry of the transition state being best represented as scheme 1:



Scheme 1

The method specially has been used for the synthesis of α,β -unsaturated carbonyl compounds by α -sulfenylation or sulfinylation of a carbonyl partner followed by pyrolysis of the corresponding α -sulfinyl carbonyl intermediate^{4,5}. The reaction is both regio controlled and stereospecific constituting a synthetically important route to α,β -unsaturated carbonyl system. The method has been used for the synthesis of chiral alkenes such as alkylidenecyclohexanes⁶.

Pyrolytic conversion of alkyl sulfoxides to olefines proceeds more sluggishly than phenyl sulfoxides and requires somewhat higher temperature for elimination. Different types of aprotic solvents (i.e. benzene, toluene dioxane, pyridine,...) have been employed. The required temperature is usually 80-120°C, and the process take several hours to proceed.

Table I. Microwave promoted β -elimination of sulfoxides

Entry	Sulfoxides	Products	Thermal Yield ^(a) 24 hrs./130°C/NMF	Microwave Yield 1 min. / NMF
1			30%	92%
2			30%	90%
3			50%	97%
4			50%	95%
5			60%	90%
6			60%	90%
7			65%	97%
8			50%	90%
9			45%	99%
10			15%	80%
11			70%	93%
12			70%	96%

a): All yields correspond to isolated pure compounds, b): Only E isomer, the Z isomer was not detected
 c): This compound is a mixture with a small amount of its tautomer.

Recently we have used N-methylformamide (NMF) as a solvent for the microwave promoted Claisen rearrangement of propargyl naphthyl ethers to naphthopyrans and naphthofurans⁷.

In this work we report the microwave promoted β -elimination of sulfenic acids from sulfoxides in NMF . We found that the irradiation of different sulfoxides⁸ in NMF as solvent in a non-modified microwave oven⁹ undergo the smooth pyrolysis in less than one minute¹⁰. The reaction is extremely fast, clean and almost quantitative yields are obtained. Table(I) summarizes the results. This method has been used for the synthesis of olefines (entries 1,2,8,10), ketones (entries 3,5,6), α,β -unsaturated carbonyl compounds (entries 7,9), and β -ketoesters.

For demonstrating the efficiency of this methodology, we also carried out the pyrolysis of the sulfoxides in thermal condition. When the sulfoxides in NMF were heated to 130°C for about 24 hours, a maximum of 70% yield were obtained (Table I). This demonstrate that the reaction by microwave irradiation proceeds about 1300 times faster.

At the end it can be concluded that, this method is quite smooth with excellent yields and compatible with alkyl or aryl sulfinyl compounds.

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8. The sulfoxides studied were all either racemic mixture or mixture of diastereoisomers. The sulfoxides **1a-c** were prepared by oxidation of the appropriate sulfides with sodium metaperiodate in aqueous methanol¹¹. The sulfoxides **2a-d** were prepared by condensation of the α -sulfinyl carbanions to the appropriate aldehydes¹². Compounds **3a-b** were synthesised by known method¹³. All compounds gave satisfactory spectroscopic data (m.pts , IR , ¹H-NMR , ...) in agreement with their structures. **Selected spectroscopic data:**
2a : m.p. 122.8°C, ¹H-NMR (80 MHz, CDCl₃), δ : 7.2-7.8 (m, 10 H, Ar), 5.35 (2xt, 1H) 5.1 (d, 1H, OH) 3.12-3.0 (dq, J_{AB}=16 Hz 17.6 Hz) , IR (CHCl₃) : 3250 , 3080 , 2880 , 2850 , 1490 , 1440 , 1070 1020 (S O) , 990 cm⁻¹; **2d** : m.p. 111.5°C, ¹H-NMR (80 MHz, CDCl₃), δ : 6.9-7.4 (m , 15H , Ar) 6.3-6.8 (m , 1H) , 5.75-6.2 (m , 1H) , 5-5.35 (m , 1H) , 3.4-3.9 (m , 1H) , IR (CHCl₃) 3276 , 3053 2923 , 1500 , 1453 , 1107 , 1030 (S O) , 976 cm⁻¹; **3a** : m.p. 126.5°C, ¹H-NMR (80 MHz CDCl₃) δ : 7.2-7.7 (m , 10H , Ar) , 5.25 (bt , 1H) , 3.6-4.2 (m , 3H) , 3.5 (d , 1H , OH) , 0.9 (t , 3H , CH₃) IR (CHCl₃) : 3430 , 3061 , 2984 , 2932 , 1730 (C O) , 1092 , 1046 (S O) , 738 cm⁻¹; **3b** : m.p. 126.5°C

$^1\text{H-NMR}$ (80 MHz, CDCl_3), δ : 7.25-7.75 (m, 6H, Ar), 6.2-6.5 (m, 2H), 5.2 (d, 1H), 3.7-4.3 (m, 3H) 1.0 (t, 3H, CH_3), IR (CHCl_3): 3349, 3000, 2923, 1738 (C O ester), 1453, 1384, 1292, 1207 1153, 1092, 1023 (S O) cm^{-1} .

9. A commercial oven AEG MICROMAT 625, 650 Watt 2450 MHz has been used.

10. **General procedure for microwave irradiation of sulfoxides**: sulfoxide (0.01 mol) dissolved in 3 ml of NMF in a teflon flask (~20 ml) and subjected to microwave irradiation for about one minute. Then the mixture was extracted with hexane (3x10 ml) after evaporation of the solvent the reaction mixture was purified by column chromatography on silica-gel.

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