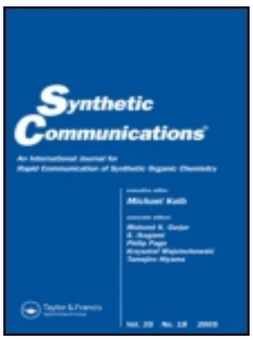

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Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Moslem M. Lakouraj , B. Movassagh & K. Ghodrati (2002) CARO's ACID SUPPORTED ON SILICA GEL. IV. FACILE SYNTHESIS OF SULFONES BY THE OXIDATION OF VARIOUS SULFIDES IN APROTIC SOLVENT, Synthetic Communications, 32:6, 847-850, DOI: 10.1081/SCC-120002692

To link to this article: http://dx.doi.org/10.1081/SCC-120002692

Published online: 16 Aug 2006.

SYNTHETIC COMMUNICATIONS, 32(6), 847–850 (2002)

CARO'S ACID SUPPORTED ON SILICA GEL. IV. FACILE SYNTHESIS OF SULFONES BY THE OXIDATION OF VARIOUS SULFIDES IN APROTIC SOLVENT

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ABSTRACT

Oxidation of sulfides with Caro's acid supported on silica gel in acetonitrile gave sulfones in high to excellent yields under mild condition.

Sulfones are important intermediates in organic synthesis,[2] which are most generally prepared either by oxidation of corresponding sulfides[3] or by a displacement reaction using sodium sulfonates as a nucleophile.[4] A number of former-type methods have been developed.[3,5] However, most of these products work well for simple sulfides, or suffer from laborious preparation of oxidizing agent, the use of potentially explosive oxidants,

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employment of heavy metal based reagents, requirement of aqueous media, or low yields, which make them synthetically unattractive.

In connection with our studies on oxidation reactions carried out with Caro's acid supported on silica gel,[1] we present here a simple, mild and efficient synthesis of sulfones by using this heterogeneous oxidizing agent.

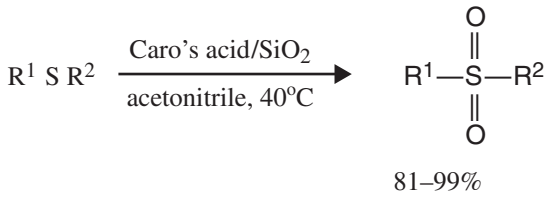

Table 1 summarizes the results obtained for a variety of sulfides which was treated with Caro's acid/SiO_2 in acetonitrile at 40°C. As evident, the use of atleast three equivalents of the oxidant is necessary to obtain sulfone as a sole product. Practically, using a lower amount of the oxidant produces a mixture of sulfoxide and sulfone, and attempts to drive the product formation exclusively toward sulfoxide are unsuccessful. A sulfoxide/sulfone selectivity of 65 : 35 is obtained in oxidation of *p*-chlorophenyl benzyl sulfide

Table 1. Oxidation of Sulfides to Sulfones with Caro's Acid/SiO_2 in CH_3CN[a]

Entry	R^1	R^2	Mol Ratio Oxid./Sub.	Reaction Time (h)	Yield[b] (%)
a	$PhCH_2$	Ph	3	5	97
b	$PhCH_2$	4-MeC_6H_4	3	5.5	96
c	$PhCH_2$	4-ClC_6H_4	3	5.5	91
d	4-$NO_2C_6H_4$	Ph	3	6.5	98
e	4-$NO_2C_6H_4$	4-MeC_6H_4	3	6.5	94
f	Ph	CH_3	3	4.5	92
g	4-MeC_6H_4	CH_3	3	5	91
h	$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	3	4.5	84
i	4-ClC_6H_4	$CH_3(CH_2)_5$	3	6.5	87
j	4-MeC_6H_4	$CH_3(CH_2)_3$	3	5.5	81
k	2,4-$(NO_2)_2C_6H_3$	4-MeC_6H_4	5	9	99

[a]Reaction carried out at reflux condition.
[b]Yields refer to the pure and isolated product.

using one molar ratio of oxidant. The method described here is easy to carry out and does not require any aqueous work-up. Yields are high to excellent, and work-up is exceedingly simple only involving filtration and evaporation.

EXPERIMENTAL

Sulfides were either prepared in our laboratory[6] or purchased from Fluka and Merck companies. All products were characterized by comparison of their spectral and physical data with those of known samples. IR spectra were obtained using a shimadzu 470 instrument. ^{1}H NMR spectra were recorded on JEOL JNM-PMX 60 MHz or Bruker 200 MHz NMR spectrometer.

Preparation of Silica gel Supported Caro's Acid

To an ice cooled 98% sulfuric acid (4.7 g) is added in small portions potassium persulfate (4.5 g) with stirring; to this is added crushed ice (13 g) and the temperature is kept below 15°C. Silica gel (5 g, Kieselgel 60G, 70–230 μm) is then added in portions to the mixture and stirred for 4 h in ice-water bath. The mixture is filtered under suction and dried in a desiccator to give a white free flowing powder.

Preparation of Benzyl Phenyl Sulfone; As a Typical Procedure

Caro's acid-silica gel (1.8 g, Caro's acid content 3 mmol),[1] is slowly added to a solution of benzyl phenyl sulfide (200 mg, 1 mmol) in acetonitrile (10 ml). The resulting mixture was stirred magnetically for 5 h at 40°C. The progress of reaction is monitored by T.L.C. (eluent: *n*-hexane/ether; 1 : 1). On completion of the reaction, the mixture is filtered. Evaporation of the solvent gave the crude product which was recrystallized from ethanol-water to afford the pure benzyl phenyl sulfone (225 mg, 97%); m.p.144–145.5°C (lit.[7] 146–146.5).

ACKNOWLEDGMENTS

The authors thank Dr. J. Ghasemi for help in analytical determination of Caro's acid and are grateful to the Razi University Research Council for the financial support of this work.

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Received in Japan December 18, 2000