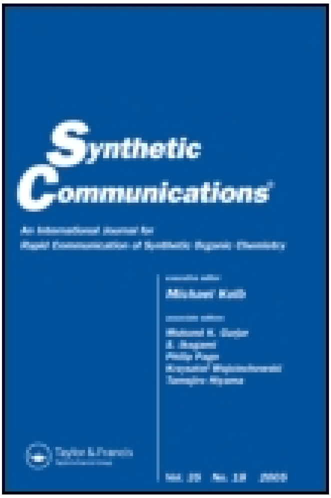

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1, 1, 1-Trifluoroacetone as an Efficient Catalyst for the Hydrogen Peroxide Promoted Selective Oxidation of Sulfides to Sulfoxides

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1,1,1-TRIFLUOROACETONE AS AN EFFICIENT CATALYST FOR THE HYDROGEN PEROXIDE PROMOTED SELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES

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Abstract. Organic sulfides are selectively oxidized to the corresponding sulfoxides in high yields and under very mild conditions using 35% hydrogen peroxide in $CHCl_3$ in the presence of catalytic amounts of 1,1,1-trifluoroacetone.

Owing to the great utility of sulfoxides in synthetic organic chemistry,[1] their formation by selective oxidation of the corresponding sulfides is one of the most important and widely studied reactions in this field, as witnessed by the numerous papers that have appeared and are still continuing to appear in the current literature.[2] The over-oxidation of the sulfoxide to the corresponding sulfone, as

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well as the Pummerer-type rearrangement, represent the main handicap in this process, so that many methods have been developed to effectively perform selective sulfide-sulfoxide conversions, many of which use sophisticated reagents or complex catalysts. Nevertheless, the simplest procedures for the oxidation of sulfides to sulfoxides make use of hydrogen peroxide, for its mildness but mainly for its non-polluting properties. However, the oxidation of sulfides by this reagent is a very slow process unless suitable solvents, such as acetone or, still better, methanol or catalysts are used.[3] Inorganic acids or acetic acid in protic solvents are efficient catalysts although they again have the disadvantage of relatively long reaction times and an easy over-oxidation to the corresponding sulfones.[4] Transition metal oxides such as V_2O_5,[5] HgO,[6] $TiCl_3$[7] as well as Selenium derivatives [8] have also been employed as efficient catalysts, even if some of them have become less attractive due to their harmful environmental impact. More recently, good reactivity and selectivity have been observed in the hydrogen peroxide-promoted oxidation of aryl methyl sulfides mediated by acetonitrile.[2d,e]

In this paper we wish to report a very simple procedure for the selective oxidation of organic sulfides in quasi-quantitative yields, under very mild conditions and over relatively short times using hydrogen peroxide in the biphasic system $H_2O/CHCl_3$ in the presence of traces of 1,1,1-trifluoroacetone as the catalyst. Results are reported in the Table. It is to be noted that, in the absence of 1,1,1-trifluoroacetone, no oxidation takes place in most cases, low amounts of sulfoxide being detected after several hours only with those substrates which have strong electron-releasing substituents bonded to the sulfur atom. Most probably the catalytic effect of 1,1,1-

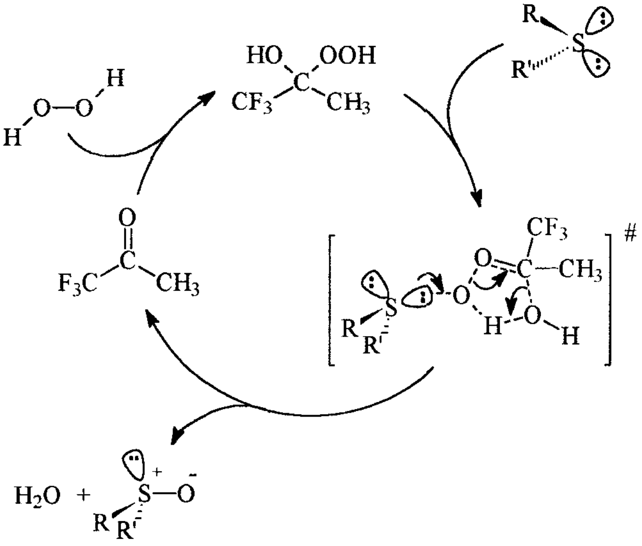
Table. 1,1,1-Trifluoroacetone Catalyzed Oxidation of Sulfides to Sulfoxides

Sulfide	t (min)	yield of sulfoxide(%)[a,b]
$^{n}Bu_2S$	15	98[c]
$\underline{CH_2CH_2SCH_2CH_2}$	15	98[c]
$^{s}BuSPh$	120	85[c]
$PhSCH_3$	90	94[d]
p-$H_3CSC_6H_4CH_2OH$	90	92[d]
$(C_6H_5)_2S$	480	96[c]
p-O_2N-$C_6H_4CH_2SC_6H_5$	300	95[d]
p-CH_3O-$C_6H_4SCH_2C_6H_5$	120	93[d]
$C_6H_5CH_2SC_6H_5$	150	90[d]
$(C_6H_5CH_2)_2S$	90	98[d]
p-H_3C-$C_6H_4CH_2CH_2SC_6H_5$	120	96[c]
$C_6H_5SCH_2COOH$	150	80[e]

[a] All sulfoxides had physical (m.p.) and spectral characteristics in agreement with literature data. [b] Yields of isolated product. [c] Isolated by chromatography on silica gel (eluent $CHCl_3$) [d] Crystallized from hexane/ether. [e] Isolated by chromatography on silica gel (eluent. 9:1 $CHCl_3/CH_3OH$).

trifluoroacetone is to be explained through the addition of the hydrogen peroxide present in the organic phase to the highly electrophilic carbonyl carbon with the consequent formation of the real oxidizing species 2-hydroperoxy-1,1,1-trifluoro-2-propanol.[9]

Owing to the powerful electron-withdrawing effect of the neighbouring trifluoromethyl group, the electrophilic peroxidic oxygen undergoes a rapid nucleophilic attack by the sulfur atom to form the expected sulfoxide and restoring, after loss of water, 1,1,1-trifluoroacetone which therefore works as an oxygen transfer agent. A cyclic transition state could be envisaged for this process such as those, by now accepted, for the oxygen transfer from benzoic peracids to the sulfur atom of an organic sulfide or to a carbon-carbon double bond in epoxidation reactions (see Scheme).



Scheme

General Procedure for the Oxidation of Sulfides to Sulfoxides. To a solution of sulfide (5.0 mmol) in $CHCl_3$ (5 mL) 35% aqueous hydrogen peroxide (0.5 mL, 5.6 mmol) and trifluoroacetone (63 mg, 0.56 mmol) were added and the mixture was vigorously stirred at room temperature (water bath) for the time indicated in the

Table. The reaction was monitored by GC-MS and t.l.c. on silica gel. The organic phase was then separated and dried with sodium sulfate. After solvent evaporation the resulting crude product was purified by crystallization or by chromatography on silica gel (eluent $CHCl_3$ or $CHCl_3$/MeOH 9/1) depending on the nature of the sulfoxide (see Table).

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