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# A Novel and Efficient Method for Oxidizing Sulfides to Sulfones with the $HOF \cdot CH_3CN$ System

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***Abstract:*** The $HOF \cdot CH_3CN$ complex, made directly by passing fluorine through aqueous acetonitrile, oxidizes all types of sulfides to the corresponding sulfones and also offering a way to make $^{18}O$ containing sulfone derivatives.

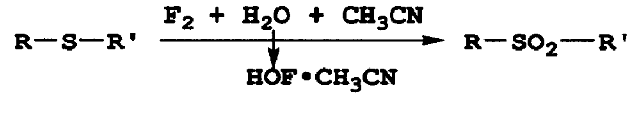
Oxidizing sulfides to sulfones is a well establish procedure. The transformation, however, requires usually lengthy treatment with oxidants which contain polluting heavy metals such as $KMnO_4$[1] or osmium tetraoxide/N-oxides[2], or the use of various peroxides, including dimethyl dioxirane[3], at high temperatures.

In the last few years we have developed a powerful oxygen transfer agent, the $HOF \cdot CH_3CN$ complex[4], made easily by passing fluorine through aqueous acetonitrile. It has proved efficient in oxidizing amines[5] and alcohols[6] using very mild conditions. We describe here a very efficient oxidation of sulfides directly to sulfones employing this non-polluting agent[7]. The reaction proceeds usually with quantitative yields, at temperatures around 0 °C in 5 - 10 minutes.

We examined several types of sulfides, all successfully oxidized. Thus 5.52 g (40 mmols) of methyl-*p*-toluylsulfide (**1**) were dissolved in 30 mL $CHCl_3$, cooled to 0 °C and added to 90 mmols of a cold (0 °C) solution of $HOF \cdot CH_3CN$ complex. After 4 minutes the oxidizing power had practically disappeared and the reaction mixture was washed with aqueous bicarbonate and then water. It was dried over $MgSO_4$ and the organic solvent removed. Methyl-*p*-toluylsulfone (**2**), mp 86 °C[8], was obtained in quantitative yield.[9]

Monitoring the reaction by GC/MS showed that already after half a minute the sulfone was formed in about 60% yield with the remaining 40% being still the starting sulfide. When only one mole of the $HOF \cdot CH_3CN$ complex was used, the reaction resulted in a 1:1 mixture of sulfone : sulfide with only traces of the corresponding sulfoxide. Even when an electron withdrawing group is on the aromatic ring as in methyl-*p*-nitrophenylsulfide (**3**) the reaction takes only a few minutes more than usual and results in the corresponding sulfone **4**, mp 142 °C[10] in quantitative yield. It should be noted, however, that the nitro group does deactivate the sulfur atom to some extent as evidenced by a competition reaction where one mole equiv. of $HOF \cdot CH_3CN$ was brought in contact with a 1:1 mixture of **1** and **3**. Both sulfones were formed, the ratio of **2** to **4** being 2:1.

A similar oxidation was observed with benzylic and cyclic sulfides such as dibenzylsulfide (5) and pentamethylenesulfide (6) which were again quantitatively transformed to the corresponding sulfones 7, mp 151 °C, and 8, mp 98 °C.[1] No special problems were encountered with very hindered sulfides either as evident from the oxidation of di-*t*-butyl sulfide (9) which formed the expected di-*t*-butyl sulfone (10) mp 130 °C[11] in a matter of minutes in 100% yield.



$$R{-}S{-}R' \xrightarrow[HOF\bullet CH_3CN]{F_2 + H_2O + CH_3CN} R{-}SO_2{-}R'$$

| | | | |
|---|---|---|---|
| 1 | R = *p*-$CH_3C_6H_4$; | R' = Me | 2 |
| 3 | R = *p*-$NO_2C_6H_4$; | R' = Me | 4 |
| 5 | R = R' = $PhCH_2$ | | 7 |
| 6 | R = R' = cyc$(CH_2)_5$ | | 8 |
| 9 | R = R' = t-Bu | | 10 |

Since the described reaction is essentially an oxygen transfer process and since, unlike most other chemical oxidations, the oxygen atom originates directly from the water, the HOF/$CH_3CN$ system presents a rare opportunity for the easy and economical labeling of the sulfone group with other than the $^{16}O$ isotope. Thus reacting 6 with the oxidative solution obtained from the action of $F_2$ on $H_2{}^{18}O/CH_3CN$ resulted in the formation of pentamethylenesulfone 8a with both oxygens of the sulfone group being the $^{18}O$ isotope (MS. m/e = 138 ($M^+$), no peaks at 136 and 134).

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