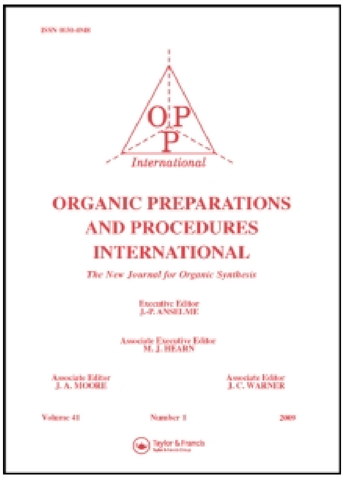

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MILD SELECTIVE OXIDATION OF SULFIDES TO SULFONES

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MILD SELECTIVE OXIDATION OF SULFIDES TO SULFONES

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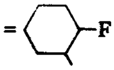
Oxidation of sulfides to sulfones can be accomplished by a variety of techniques including hydrogen peroxide,[1] peracid,[2] or chromic acid.[3] One report describes the selective oxidation of sulfides containing amine and alkene functionality with peroxytrifluoroacetic acid;[2] however, caution must be exercized to ensure complete decomposition of the peracid. This caution and interference from functional groups such as carbon-carbon double bonds[4] has prompted us to develop a procedure employing periodate and permanganate under neutral conditions. Unlike the Lemieux-von Rudolff reagent[5] which uses a catalytic amount of permanganate in the presence of sodium periodate, the method herein described requires one equivalent each of periodate, permanganate and sulfide. The periodate oxidizes the sulfide to the sulfoxide which is then converted to the sulfone by the permanganate. Sulfoxides are more reactive with permanganate than sulfides.[6] After the reaction is complete the inorganic by-products are easily removed by filtration.

$$\underset{\underline{1}}{RSR'} \xrightarrow[KMnO_4\text{-}MgSO_4]{NaIO_4} \underset{\underline{2}}{RSO_2R'}$$

a) R = R' = $PhCH_2$ b) R = Ph, R' = CH_3 c) R = Ph, R' = CH_2=$CHCH_2$

d) R = Ph, R' = CH_3CH=$CHCH_2$ e) R = Ph, R' = H_2NCOCH_2

f) R = Ph,R' = HO_2CCH_2 g) R = Ph, R' = $HOCH_2CH_2$ h) R = Ph, R' = 

Alkenic double bonds, alcohols, amides and carboxylic acid functions do not interfere in this reaction. Although periodate has been used as a co-oxidant with permanganate for cleavage of carbon-carbon double bonds, the oxidation of sulfides occurs more readily and the double bond is not affected. By contrast, 3-methyl-2-butenyl phenyl sulfide gives no sulfone on oxidation with benzyltrimethylammonium permanganate.[4] Hydroxyl groups have been shown to react slowly with periodate containing a catalytic amount of permanganate;[7] however, under the conditions described here no reaction is observed. Electron-withdrawing groups in the sulfide tend to retard severely the rate of reaction. The β-fluorosulfide required 10 hrs reflux for complete oxidation. While no attempt was made to optimize the yields, they compare favorably with other methods of sulfide the oxidation. For example, dibenzyl sulfone is prepared in only 24% yield from the CrO_3 oxidation of the corresponding sulfide.[3] Further, the yields for oxidation of α-alkylmercapto amides to α-alkylsulfonylamides with H_2O_2 average 72%.[1]

EXPERIMENTAL SECTION

General Procedure.- To a solution of the sulfide (1, 3.0 mmol) in acetone (20-30 ml) containing magnesium sulfate (ca. 2 g), was added dropwise sodium periodate (0.642 g, 3 mmol) and potassium permanganate (0.316 g, 2 mmol) in 25 ml water with stirring. A brown precipitate formed and stirring was continued until the mixture turned colorless; then sodium metabisulfite (ca. 3 g) was added; the solution became yellow within minutes. The solution was filtered and extracted with methylene

TABLE 1. Sulfones Prepared from $NaIO_4$-$KMnO_4$ and Sulfide

2	Yield (%)	IR SO_2 (cm^{-1})	Time (hrs.)	bp/torr or(mp.)(°C)	Lit. (°C)
a	91	1120 1320	72	(150.5-152)	(150)[a]
b	91	1150 1300	2	(86-87)	(88)[b]
c	80	1150 1325	2	115/0.4	110-113/0.5[c]
d	84	1140 1320	3	134-8/0.5	106-109/0.1[d]
e	79	1150 1310	24	(154-155)	(153)[e]
f	93	1155 1330	2	(110-112)	(111.5-112.5)[f]
g	83	1140 1300	6	154/0.5	190/4[g]
h	75[h]	1150 1300	i	(49)	---

a) Beil., 6, H 456 b) Beil, 6, H 297 c) Beil., 6, IV 1480 d) Beil., 6, IV 1481 e) Beil., 6, H 315 f) Beil., 6, H 314 g) Beil., 6, IV 1494 h) Anal. Calcd for $C_{12}H_{15}FSO_2S$: C, 59.48; H, 6.24; S, 13.23. Found: C, 59.30; H, 6.26; S, 13.16 i) Ten hrs. reflux chloride (40 ml). A saturated sodium chloride solution (30 ml) was added to the CH_2Cl_2 extracts. The sodium chloride solution was then reextracted twice with methylene chloride (40 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated to give the crude sulfone. Analysis by TLC and NMR confirmed that the sulfide had been consumed. The known sulfones were purified by vacuum distillation or recrystallization and characterized by NMR and IR. The percent yields and physical properties are reported in Table 1.

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INDIRECT IODINATION WITH 2-(3,5-DIIODO-4-METHOXYPHENYL)-1,3,4-OXADIAZOLE AS A PRECURSOR OF AN AROYL HYDRAZINE

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Iodinated contrast enhancement agents are frequently used to add