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A SELECTIVE AND CONVENIENT OXIDATION OF SULFIDES TO SULFOXIDES WITH FERRIC NITRATE AND SILICA GEL

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A SELECTIVE AND CONVENIENT OXIDATION OF SULFIDES TO SULFOXIDES WITH FERRIC NITRATE AND SILICA GEL

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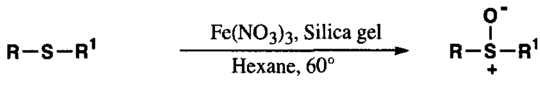
The selective oxidation of sulfides to sulfoxides is an attractive and extremely important method, since sulfoxides are useful building blocks in organic synthesis.[1] The clay-supported ferric and cupric nitrates-based biphasic methods of Cornelis and Laszlo[2] (termed "*Clayfen*" and "*Claycop*" for short, respectively) have shown good selectivity in the oxidation of many classes of organic compounds; however, no investigation has been carried out on the oxidation of sulfide, despite the successful application of these reagents to the oxidation of sulfur compounds such as thiols and thioacetals.[2] We recently reported the convenient oxidation of benzylic and aliphatic alcohols to carbonyl compounds with *in situ* generated Montmorillonite K10-supported ferric nitrate reagent in hexane.[3] In comparison to the method using *Clayfen*, our procedure is easier and safer to perform and gives in certain cases higher yields than those reported with *Clayfen*. Encouraged by this success and in view of the lack of studies on sulfide oxidation with *Clayfen*, we have tested the *in situ* method for the oxidation of sulfides.

Preliminary experiments showed that although the ferric nitrate oxidation of sulfides proceeds smoothly in the presence of Montmorillonite K10,[3] the isolation of the sulfoxides presents a serious problem. This is presumably due to their adsorption on the clay because of their high polarity, thus leading to decreased yields. In addition, depending on the sulfide, the clay sometimes aggregated to form an intractable solid mass leading to inefficient agitation of the reaction mixture; as a consequence, the reaction is not reproducible and this method is essentially impractical. Accordingly, we sought for a more efficient support material. Among the supports examined (aluminas, aluminum sili-



1 2

a) R=Ph, R^1=Me
b) R=p-MeOC$_6$H$_4$, R^1=Me
c) R=p-MeC$_6$H$_4$, R^1=Me
d) R=p-ClC$_6$H$_4$, R^1=Me
e) R=p-BrC$_6$H$_4$, R^1=Me
f) R=p-NO$_2$C$_6$H$_4$, R^1=Me
g) R=p-CHOC$_6$H$_4$, R^1=Me
h) R=Ph, R^1=Et
i) R=Ph, R^1=n-Pr
j) R=Ph, R^1=i-Pr
k) R=Ph, R^1=n-Bu
l) R=Ph, R^1=n-C$_6$H$_{13}$
m) R=Ph, R^1=Ph
n) R=Ph, R^1=PhCH$_2$
o) R=PhCH$_2$, R^1=PhCH$_2$
p) Thianthrene
q) R=n-Pr, R^1=n-Pr
r) R=i-Pr, R^1=i-Pr
s) R=n-Bu, R^1=n-Bu
t) R=s-Bu, R^1=s-Bu
u) R=n-C$_8$H$_{17}$, R^1=Me
v) Tetrahydrothiophene
w) Tetrahydrothiopyran

cate, silica gel, clay minerals, florisil, zeolites), we chose silica gel for the present purpose, owing to the ease of reaction, and to the selectivity and yield of sulfoxides. Solvent, reaction temperature, and the amount of silica gel also played important roles in this oxidation. For example, as in the previous case,[3] hexane was found to be a superior (conversion of PhSMe **1a** and selectivity of PhSOMe **2a** were 100 and 95%, respectively) to CH_2Cl_2 (68 and 97%), $CHCl_3$ (90 and 93%), CCl_4 (88 and 89%), AcOEt (62 and 65%), MeCN (100 and 90%), EtOH (2 and 100%), benzene (100 and 76%) and ether (14 and 100%). Thus the oxidation of sulfides was carried out in hexane, at 60° by utilizing the optimum amount of ferric nitrate and chromatographic silica gel and running the reaction to 100% conversion except for *p*-nitrophenyl methyl sulfide **1f** (*vide* TABLE 1).

Although the ease of the reactions is dependent on the electrosteric properties of the sulfides, it should be emphasized that the reactions can be performed cleanly and controlled to stop at the sulfoxides stage; there was no evidence for the formation of any sulfones which enabled easy isolation of the sulfoxides. Nishiguchi and his co-workers have claimed that metal nitrates, including ferric salts, were inactive for the oxidation of alcohols[4a] and the oxidative cleavage of ethers[4b] when they are not supported on silica gel, but only mixed with the latter. Similarly, Laszlo *et al.*[5] have pointed out that silica gel impregnated with ferric nitrate has no oxidative capacity. However, the applicability of the present procedure for a wide range of alkyl aryl, diaryl, dialkyl and cyclic sulfides produced the corresponding sulfoxides in good to nearly quantitative yields. These results in combination with the operational simplicity of the procedure constitute a useful, and economically and environmentally acceptable alternative to the currently available methodologies.

EXPERIMENTAL SECTION

The ^1H NMR spectra were recorded with a JEOL PMX-60 (60 MHz) spectrometer using deuteriochloroform solution with TMS as an internal standard. The IR spectra were measured on a JASCO A-100 spectrophotometer as thin films (neat) or KBr disks. Analytical gas chromatography was performed on a Shimadzu GC-4CM instrument equipped with a flame ionization detector through a 2 mx5mmØ glass column packed with 3% Silicone OV-17 on Uniport HP (60-80 mesh) and interfaced with a Shimadzu Chromatopac C-E1B integrator, with temperature programming. Melting points were determined on a Yanagimoto MP-S3 melting point apparatus and were uncorrected. Fuji-Davison Silica Gel BW-300 and Merk Silica Gel 60 were used for the preparative reaction and column chromatography, respectively. Ferric nitrate nonahydrate and sulfides, except for propyl phenyl, isopropyl phenyl, butyl phenyl and hexyl phenyl sulfides, were obtained from commercial sources and were used as received. The other four sulfides were synthesized from thiophenol and the corresponding alkyl bromides in benzene in the presence of DBU.[6] The purities of all sulfides were checked by GC just before use. Solvents were dried and distilled prior to use.[7]

General Oxidation Procedure.- The following procedure for methyl phenyl sulfide **1a** is representative. A 30 mL two-necked round-bottom flask, equipped with a stir bar, a 25 cm reflux condenser and a glass tubing connected to an argon-filled balloon, was arranged for conducting the reaction under inert atmosphere by connecting the top of the condenser to a liquid paraffin trap in order to exclude air

TABLE 1. Oxidation of Sulfides with Ferric Nitrate[a]

Sulfoxides	$Fe(NO_3)_3$ (mmol)	Silica gel (g)	Time (hrs)	Yield (%)	mp (°C) or bp (°C/torr) Found	Reported
2a	0.6	0.9	1	85	32-33	33-34[d]
2b	0.35	0.9	0.17	91	43-44	44[e]
2c	0.5	0.9	0.5	88	42-43	41-42[f]
2d	0.6	1.5	1	88	46-47	47-48[f]
2e	0.6	0.9	2.5	86	83-84	82.5-84[f]
2f[b]	2.0	1.5	4	83	147-148	147-148[f]
2g	2.0	1.5	4	90	80-82	81-82[g]
2h	1.0	2.0	1	90	80-83/0.15	146/13[d]
2i	1.5	2.0	1	94	90-94/0.1	102-103/0.01[d]
2j	2.0	2.0	1	84	95-98/0.04	97-100/0.01[e]
2k	1.5	2.0	1	91	98-100/0.4	95/0.01[h]
2l	1.5	2.0	1	86	108-111/0.1	105-110/0.09[h]
2m	1.0	2.0	1	84	69-70	70.5[d]
2n	0.35	2.0	1	87	122-124	125.5[d]
2o	1.5	0.9	2	86	134-135	133-135[d]
2p	1.0	0.9	1	96[c]	143-144	143-144[d]
2q	1.5	0.9	1	87	73-75/1	75/0.5[i]
2r	2.0	2.0	1	88	59-61/3	87/15[i]
2s	1.5	0.9	1	90	95-97/2	72/0.5[i]
2t	2.0	2.0	5	85	73-75/1	65/0.5[i]
2u	1.0	0.9	1	83	40-41	40-40.5[j]
2v	0.35	0.9	1	72	95-98/3	89/0.5[i]
2w	0.9	0.9	1	81	67-68	66-67[i]

a) At 60°, under argon; sulfide 1 mmol, hexane 10 mL. *b*) 11% of **1f** was recovered. *c*) Thianthrene 5-oxide was the only product formed. *d*) *Dictionary of Organic Compounds*, Chapman & Hall (London), 6th ed (1966). *e*) G. Barbieri, M. Cinquini, S. Colonna & F. Montanari, *J. Chem. Soc. (C)*, **1968**, 659. *f*) R. W. Murray, R. Jeyaraman & M. K. Pillay, *J. Org. Chem.*, **52**, 746 (1987). *g*) X. Creary & M. E. Mehrsheikh-Mohammadi, *J. Org. Chem.*, **51**, 1110 (1986). *h*) D. Jahnke & H. Reinheckel, *Organometal. Chem. Synth.*, **1**, 31 (1970/1971); for **2l**, see also, H. Reinheckel & D. Jahnke, *Chem. Abstr.*, **66**, 104821X & **67**, 73356P (1967). *i*) K. Orito, T. Hatakeyama, M. Takeo & H. Suginome, *Synthesis*, **1995**, 1357. *j*) D. Jerchel, L. Dippelhofer & D. Renner, *Chem. Ber.*, **87**, 947 (1954).

oxidation. In the flask were placed methyl phenyl sulfide (0.124 g, 1 mmol), hexane (10 mL), and finely pulverized ferric nitrate nonahydrate (0.242 g, 0.6 mmol) in that order and stirring was started. After addition of silica gel (0.9 g), a gentle stream of the argon was passed through the system. The resultant heterogeneous mixture was vigorously stirred for 1 hr at 60°. The reaction mixture was filtered through a sintered glass funnel and the filter cake was thoroughly washed with portions of dichloromethane (*ca.* 100 mL). Rotary evaporation of the combined filtrate *in vacuo* left an oil, which was immediately chromatographed on a silica gel column (*Merk 60*) by elution with a mixture of hexane and ethyl acetate (6:4 by volume) to afford pure (GC, TLC and NMR) methyl phenyl sulfoxide **2a** (0.119 g, 85%).

Oxidations of the other sulfides were carried out as above, and the identities of the resultant sulfoxides were derived from spectral comparison (^{1}H NMR and IR) with authentic samples synthesized independently.

REFERENCES

1. For reviews on the oxidations of sulfides to sulfoxides, see: M. Madesclaire, *Tetrahedron*, **42**, 5459 (1986); J. Drabowicz and M. Mikolajczyk, *Org. Prep. Proced. Int.*, **14**, 45 (1982); M. Hudlicky, *Oxidations in Organic Chemistry*, Am. Chem. Soc., Washington, DC (1990), p. 252-259.
2. A. Cornelis and P. Laszlo, *Synthesis*, 909 (**1985**).
3. M. Hirano, K. Komiya and T. Morimoto, *Org. Prep. Proced. Int.*, **27**, 703 (1995).
4. a) T. Nishiguchi and F. Asano, *J. Org. Chem.*, **54**, 1531 (1989); b) T. Nishiguchi and M. Bougauchi, *ibid.*, **55**, 5606 (1990).
5. A. Cornelis, P. Laszlo and P. Pennetreau, *Bull. Soc. Chim. Belges*, **93**, 961 (1984).
6. N. Ono, H. Miyake, T. Saito and A. Kaji, *Synthesis*, 952 (**1980**).
7. *Techniques of Chemistry*, Vol. II, *Organic Solvents*, 3rd. ed, ed by J. A. Riddick and W. B. Bunger, Wiley-Interscience, New York (1970).

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