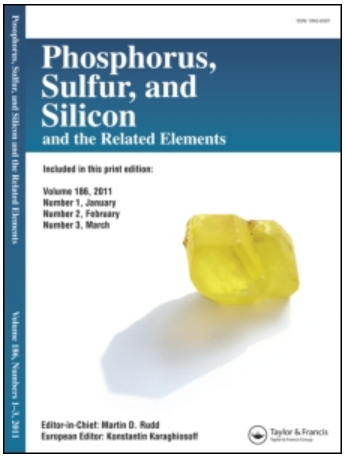

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Selective Oxidation of Sulfides to Sulfoxides by Atmospheric Oxygen and Aldehyde Catalysed by NI^{II} Complexes

Stephane Vincent[a]; Claude Lion[a]; Mir Hedayatullah[a]; Anthony Challier[a]; Gerard Delmas[b]; Gilbert Magnaud[b]

[a] Université Denis Diderot Paris VII, associé au CNRS URA 34 1, Paris, France [b] Ministère de la Défense Nationale, Centre d'Etudes du Bouchet, Vert-Le-Petit, France

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SELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES BY ATMOSPHERIC OXYGEN AND ALDEHYDE CATALYSED BY NI^{II} COMPLEXES

STEPHANE VINCENT, CLAUDE LION,* MIR HEDAYATULLAH and ANTHONY CHALLIER

Université Denis Diderot Paris VII, associé au CNRS URA 34
1, rue Guy de la Brosse 75005 Paris, France

and

GERARD DELMAS and GILBERT MAGNAUD

Ministère de la Défense Nationale, Centre d'Etudes du Bouchet B.P. 3 91710 Vert-Le-Petit, France

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A new and efficient method for oxidising sulfides selectively to sulfoxides has been developed with atmospheric oxygen, in the presence of isobutyraldehyde and catalysed by Ni^{II} complexes such as bis[1,3-bis-(p-methoxyphenyl)-1,3-propanedionato]nickel, $[Ni(dmp)_2]$, and bis[acetylacetonato]nickel, $[Ni(acac)_2]$.

Key words: Sulfides, oxidation, sulfoxides, oxygen, Ni complexes.

INTRODUCTION

The oxidation of sulfides to sulfoxides and sulfones is a well known and a much studied reaction.[1] It generally requires oxidants such as hydrogen peroxide, peracids or oxaziridines.[1,2]

During recent years, much work has been directed towards the search for specific oxidising agents which are both cheap and avoid the hazardous use of compounds such as m-choro-peroxybenzoic acid (mCPBA). Processes involving molecular oxygen have also been developed but these catalysed reactions need relatively drastic conditions of pressure and temperature.[1,3]

In this paper we describe a new, simple, selective and often quantitative method for oxidising thioethers to sulfoxides by molecular oxygen, at atmospheric pressure, in the presence of an aldehyde and catalysed by a Ni^{II} complex.

This reaction is an extension to sulfides of a recently published method for oxidising olefins and ketones[4] (Equation 1).

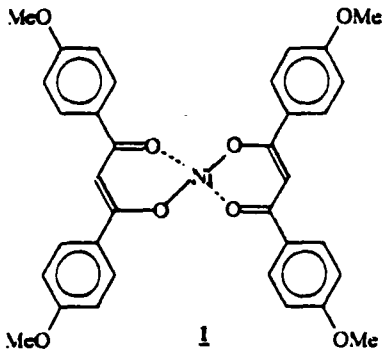
$$R_2S + R'CHO \xrightarrow[Ni^{II}]{O_2} R_2SO + R'CO_2H \qquad (1)$$

We have determined the optimal conditions for this reaction: the importance of the structure of the aldehyde, effects of solvent and temperature, the nature of the catalyst and the thioether.

RESULTS AND DISCUSSION

Structure of the Catalyst

Sulfide oxidation by molecular oxygen catalysed by Ni^{II} complexes has not been much studied, although the reaction is well described with complexes of vanadium, molybdenum or chromium.[3c,4c] Our results show that the complexes bis[1,3-(p-methoxyphenyl)-1,3-propanedionato]nickel, $Ni(dmp)_2$ **1**, and bis[acetylacetonato]-nickel, $Ni(acac)_2$ **2**, allow the oxidation of thioethers in the presence of aldehyde. We have improved the reaction with di-n-butyl sulfide and isobutyraldehyde (Table I). $Ni(dmp)_2$ **1** is more effective than $Ni(acac)_2$ **2**, as had been shown for the epoxidations[4a,b] (expt. 1 and 3). Consequently all experiments were carried out with $Ni(dmp)_2$ **1**.



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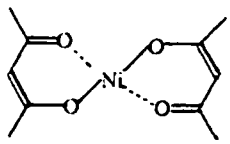


2

Importance of the Structure of the Aldehyde

The reaction has been tested with different aromatic and aliphatic aldehydes. The latter, oxidised by molecular oxygen, would give a "peroxyacidic-like" molecule which would oxidise the sulfur[4a,b] (the mechanism has not been much studied and remains unclear). As for the epoxidation,[4a,4b] only the aliphatic aldehyde leads to

TABLE I

Oxidation of di-n-butyl sulfide by atmospheric oxygen, at 60°C, in presence of an aldehyde RCHO, and catalysed by a complex of Ni^{II}.[a]

expt.	catalyst	RCHO	Time(h)	Solvent	yield(%)
1	**1**	i-PrCHO	18	MeCN	100
2	**2**	i-PrCHO	28	MeCN	49
3	**2**	i-PrCHO	48	MeCN	81
4	**1**	i-PrCHO	15	AcOEt	99
5	**1**	C_6H_5CHO	24	AcOEt	0
6	**1**	i-PrCHO	18	Toluene	85[b]
7	**1**	i-PrCHO	21	EtOH	32
8	**1**	i-PrCHO	21	EtOH/H_2O (9/1)	9
9	**1**	i-PrCHO	17	$ClCH_2CH_2Cl$	72[b]

(a) For the proportions of reactants see Experimental section.
(b) Total conversion, the sulfone is the only by-product.

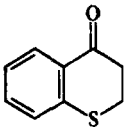
TABLE II

Oxidation of thioethers with $Ni(dmp)_2$ 1, atmospheric oxygen, isobutyraldehyde, in acetonitrile.[a]

expt.	sulfide	T (°C)	Time (h)	Yield (%)
10	Ph_2S	24	2	85[b]
11	PhSMe	24	14	66[b]
12	$(PhCH_2)_2S$	60	18	100
13	Tetrahydrothiophene, 3	60	25	98
14	$PhCH_2CH_2SCH_2CH_2Cl$, 5[5]	60	18	100
15	Et_2S	60	21	100
16	CH_2=CHSMe	60	26	87[b]
17	Thiochroman-4-one, 4	60	20	75[b]

[a] For reactant proportions see Experimental section.
[b] Total conversion, the main by-product is the sulfone.

Tetrahydrothiophene 3



Thiochroman -4-one 4

the oxidation of sulfides to sulfoxides. Some results are listed in Table I (expt. 4 and 5).

Solvent Effect

Experiments, performed with different solvents (protic, aprotic, polar and apolar) show that solvents such as acetonitrile or ethyl acetate which are easy to use, give excellent results whereas protic solvents like ethanol, methanol and ethanol-water decrease the efficiency of this oxidising system. It appears that drying the complex (especially $Ni(acac)_2$ 2) by azeotropic distillation before the reaction, increases the rate of the reaction dramatically.

Reactivity of Different Thioethers

The oxidation by atmospheric oxygen of di-n-butyl sulfide is optimal at 60°C, with isobutyraldehyde and $Ni(dmp)_2$. 1. The reaction is quantitative in 18 hours. We therefore applied these conditions for most of the different studies listed in Table II.

Surprisingly, the oxidation of aromatic sulfides (expt. 10 and 11) occurs faster and in milder conditions of temperature than for the aliphatic ones (the latter do not react at room temperature). On the other hand, if the reaction is stopped early enough, the aliphatic sulfides give exclusively the sulfoxide in often quantitative yields (expt. 12 to 15). In the case of the chloro sulfide (expt. 14), we can appreciate the possibilities offered by this reaction for the destruction of the particular toxic sulfur compounds of the vesicant family.[5] We showed too the good chemoselectivity of the reaction (expt. 16 and 17) for which epoxidation and the Baeyer-Villiger reaction are largely minimised.

To conclude, an easy, mild and efficient method for oxidising thioethers to sulfoxides by atmospheric oxygen in the presence of isobutyraldehyde and catalysed by a Ni^{II} complex has been developed.

EXPERIMENTAL

$Ni(dmp)_2$ **1** was synthesised by Mukaiyama's method[4b]; $Ni(acac)_2$ **2** was a commercial product. The aldehydes (stored under argon) and the sulfides were commercial products (except sulfide **5** synthesised by the method previously described[5]) and were used without further purification. The solvents were used anhydrous.

Typical procedure. The mixture of the sulfide, the aldehyde (3 equivalents at room temperature, 5 equivalents when the medium was warmed), the complex (3 mol%) and the solvent (enough to obtain 1.5 M sulfide) was vigorously stirred in an open flask (equipped of a reflux condenser if the mixture was warmed). At the end of the reaction the mixture was concentrated, then diluted in a small quantity of CH_2Cl_2 and washed 3 times with aqueous Na_2CO_3. The organic layer was dried ($MgSO_4$), filtered and concentrated. The sulfoxide is isolated by filtration on a short column of silica gel.

Following of the reaction and analysis. All experiments were followed by gas chromatography, the retention times being compared with those of commercially available compounds. The products of the reaction were analysed by GC-MS and the mass spectra compared with those of commercial sulfoxides and sulfones. When the products were not commercial, we compared IR, NMR and mass spectra with literature data or with the spectra of sulfoxides and sulfones synthesised by oxidation with m-chloroperoxybenzoic acid.

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REFERENCES

1. M. Madesclaire, *Tetrahedron*, **42,** 5459 (1986) and references therein.
2. Y. Chang, L. L. Szafraniec and W. Beaudry, *J. Org. Chem.*, **55,** 3664 (1990); D. D. DesMarteau, V. A. Petrov, V. M. Montanari, M. Pregnolato and G. Resnati, *J. Org. Chem.*, **59,** 2762 (1994).
3. a) D. P. Riley, M. R. Smith and P. E. Correa, *J. Am. Chem. Soc.*, **110,** 177 (1988); b) P. E. Correa, G. Hardy and D. P. Riley, *J. Org. Chem.*, **53,** 1695 (1988); c) A. V. Mashkina, *Catal. Rev.-Sci. Eng.*, **32,** 105 (1990) and references therein.
4. a) P. Laszlo and P. Levart, *Tetrahedron Letters*, **34,** 1127 (1993); b) T. Yamada, T. Takai, O. Rhode and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **64,** 2109 (1991); c) M. Hamamoto, K. Nakayama, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, **58,** 6421 (1993).
5. A. Leblanc, C. Lion, G. Magnaud, G. Delmas and C. Charvy, *Phosphorus, Sulfur and Silicon*, **79,** 141 (1993).