



Oxidation of Organic Sulphides to Sulphoxides by Nitric Acid Catalyzed by FeBr_3 and $(\text{FeBr}_3)_2(\text{DMSO})_3$.

Angela R. Suárez*; Laura I. Rossi and Sandra E. Martín.

Departamento de Química Orgánica. Facultad de Ciencias Químicas.

Universidad Nacional de Córdoba. Suc. 16, C.C. 61. (5016)

Córdoba. ARGENTINA.

Abstract : The selective oxidation of organic sulphides to sulphoxides by 9.5 % (~1.5 M) nitric acid was catalyzed by FeBr_3 and the coordination compound $(\text{FeBr}_3)_2(\text{dimethylsulphoxide})_3$.

Since alkyl sulphoxide derivatives can serve as non-functional as well as anionic synthons,¹ preparation of these compounds by efficient methods are of continuous interest in organic chemistry.² We now report the results of a comparative study of the catalytic activity of FeBr_3 and the coordination compound $(\text{FeBr}_3)_2(\text{DMSO})_3$, **1**, where DMSO = dimethylsulphoxide, in the selective oxidation of organic sulphides to sulphoxides. Compound **1** result very inexpensive as catalyst owing to its high stability and also because of its high activity and selectivity in these reactions. Furthermore, the starting FeBr_3 is not an expensive reagent. This work is part of our research on the catalytic activity of compounds of the type $(\text{MX}_n)_m(\text{L})_l$, where M is a 3d transition metal or aluminum; X = Cl or Br and L are organic ligands. In those cases where the anhydrous salts are necessary as catalysts, the main advantage of the use of these coordination compounds is their high stability to moisture in opposition to the parent halides.

A series of coordination products of DMSO to iron and other transition metal halides have been known since 1960.³⁻⁸ To the best of our knowledge, the only reports on their applications in organic synthesis are the sulphide oxidations catalyzed by $\text{RuX}_2(\text{DMSO})_4$, X = Cl, Br.⁹⁻¹³ Commonly, alkyl sulphoxides are prepared by oxidation of the corresponding sulphides with different oxidants.² In this work we employed a dilute solution of nitric acid (9.5% v/v; ~ 1.5 M). Concentrated nitric acid, specific gravity 1.3-1.4, has been earlier employed as oxidant of organic sulphides to sulphoxides with the advantage of economy over other oxidizing agents.^{14,15} A 1.6 M solution of nitric acid was used in reactions catalyzed by tetrabutylammonium tetrahaloaurate(III).¹⁶

The reactions herein were carried out in a biphasic system consisting of an aqueous layer formed by 16 ml of a nitric acid solution containing the catalyst and an organic phase consisting of a solution of the substrate (5 mmol) in 16 ml either of nitromethane or dichloromethane. The substrate:catalyst ratio was 10:1. The reactions were performed either at room temperature or at 40 °C under continuous

stirring and followed by TLC on silica gel with ethyl acetate or ethylacetate:benzene (60:40) as developing solvents.

The substrates were di-*n*-butyl sulphide, **2a**, methyl phenyl sulphide, **3a**, and benzyl phenyl sulphide, **4a**. The products were identified as di-*n*-butyl sulfoxide, **2b**, methyl phenyl sulfoxide, **3b** and benzyl phenyl sulfoxide, **4b**, by their IR, ¹H NMR spectra (200 MHz), rf, m.p. and mixed m.p. in the case of **4b**. Although solids, **2b** and **3b** are very hygroscopic and their m.p. could not be determined. Only the starting sulphides were detected in the reactions performed without catalyst. The reaction conditions and yields are collected in Table 1. The reaction is schemed in equation (1)

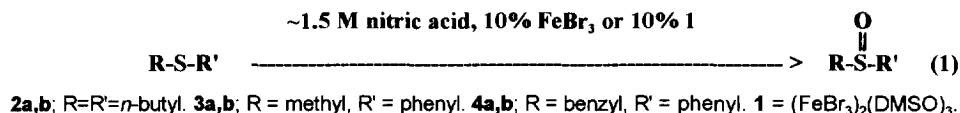


TABLE 1: Oxidation of organic sulphides to sulfoxides with ~1.5 M nitric acid and a 10% mol of catalyst.^a

Substrate	Catalyst	Solvent	Time (min)	Product	Yield % ^b	m.p. ^c °C
2a	FeBr ₃	CH ₃ NO ₂	30	2b	84	-
"	1	"	120	N.R.	-	-
"	"	"	60 ^d	2b	88	-
"	FeBr ₃	CH ₂ Cl ₂	60	"	96	-
"	1	"	120	"	99	-
"	"	"	45 ^d	"	84	-
3a	FeBr ₃	CH ₃ NO ₂	60	3b	58	-
"	1	"	75	"	78	-
"	FeBr ₃	CH ₂ Cl ₂	120	"	65	-
"	1	"	120	"	81	-
4a	FeBr ₃	CH ₃ NO ₂	30	4b	77	124-125
"	1	"	45	"	80	124-124.5
"	FeBr ₃	CH ₂ Cl ₂	120	"	93	122-123
"	1	"	120	"	91	120-122

a: At room temperature unless other data are reported. b: Product isolated from the organic layer. c: Melting points correspond to the crude product from the organic layer. N.R.: Reaction did not occur. d: Reactions at 40°C.

The reported yields corresponded to the crude products isolated from the organic layer after drying and vacuum evaporation of the solvent. The reaction mixture compositions were evaluated by ^1H NMR. Authentic samples of the corresponding sulfoxides and sulphones were used for identification purposes.

In general, reactions carried out with **1** as the catalyst gave higher yields, despite the fact that they took more time to complete than those performed with FeBr_3 . TLC analysis demonstrated that there was an induction period before the reactions catalyzed by **1** started. These results could be explained if, as has been proposed in reactions catalyzed by ruthenium halide complexes with DMSO, the organic sulphide should coordinate to the metal prior to oxidation.⁹ In those cases where the catalyst was **1**, the substrate should displace a DMSO ligand before coordination.

In Table 2 are shown the results of an additional test carried out under similar conditions in order to compare the catalytic ability of FeBr_3 and **1**. The reactions were performed by recycling the aqueous phase containing the oxidant as well as the catalyst while the organic phase with substrate **4a** was renewed. The organic solvent employed was dichloromethane.

TABLE 2: Consecutive oxidation cycles of **4a** to **4b** without changing the aqueous layer.^a

Cycle	Catalyst	4a (%)	4b (%)	m.p. °C ^b
1	FeBr_3	Traces	87	122-123
2	"	"	87	121-123
3	"	5	88	116-122
4	"	40	48	81-101
5	"	49	37	38-90
6 ^c	"	52	24	37-89
1	1	Traces	88	121-122
2	"	"	86	121-122
3	"	12	76	105-112
4	"	25	63	93-108
5	"	52	27	37-89
6 ^c	"	34	52	85-109

a: The reaction time was 2 h unless other data are reported. b: melting points of the crude product from the organic layer. c: the reaction time was 8 h.

The yields shown in Table 2 were calculated from the crudes obtained from the organic layer and

from the ^1H NMR evaluation of their compositions. Reported melting points also correspond to the crudes from the organic layer. As can be seen, the catalytic activity of **1** was more prolonged than that of FeBr_3 .

In summary, we report herein a new and efficient method for the selective oxidation of sulphides to sulfoxides under very mild conditions.

Acknowledgement: We are grateful to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba (CONICOR), Argentina for financial support. L. I. R. and S. E. M. also thank CONICET for fellowships.

References

1. Fuhrhop, J. and Penzlin, G. *Organic Synthesis. Concepts, Methods, Starting Materials*. 2nd Edition. V.H.C., Weinheim. **1994**. Pages 8-9, 45, 51, 75-76, 154.
2. Hudlicky, M. *Oxidations in Organic Chemistry*. ACS Monograph 186. American Chemical Society. Washington, DC. **1990**. Pages 252-259, 281, 287-288, 294 and references cited therein.
3. Cotton, F. A. and Francis, R. *J. Am. Chem. Soc.*, **1960**, 82, 2986.
4. Drago, R. S.; Meek, D. W. and Straup, D. K. *J. Am. Chem. Soc.*, **1960**, 82, 6013.
5. Selbin, J.; Bull, W. E. and Holmes Jr., L. H. *J. Inorg. Nucl. Chem.*, **1961**, 16, 219.
6. G. Wilkinson; J. D. Gilbert and D. Rose. *J. Chem. Soc. A*, **1970**, 2765.
7. James, B. R.; Ochiai, E. and Rempel, G. I. *Inorg. Nuclear Chem. Letters*, **1971**, 7, 781.
8. Wilkinson, G.; Evans, I. P. and Spencer, A. *J. Chem. Soc. Dalton Trans.*, **1973**, 204.
9. Riley, D. P. and Oliver, J. D. *Inorg. Chem.*, **1986**, 25, 1814.
10. Riley, D. P. and Oliver, J. D. *Inorg. Chem.*, **1986**, 25, 1821.
11. Riley, D. P. and Oliver, J. D. *Inorg. Chem.*, **1986**, 25, 1825.
12. Riley, D. P. and Lyon III, J. *J. Chem. Soc., Dalton Trans.*, **1991**, 157.
13. Mestroni, G.; Srivastava, R. S.; Milani, B. and Alessio, E. *Inorganica Chimica Acta*, **1992**, 191, 15.
14. Grabowsky, N. *J. Liebigs Ann. Chem.*, **1875**, 175, 848.
15. Beckmann, O. *J. Prakt. Chem. (2)*, **1878**, 17, 471.
16. Gasparini, F.; Giovanoli, M.; Misiti, D.; Natile, G.; Palmieri, G. *J. Org. Chem.*, **1990**, 55, 1323. And references cited therein.

(Received in USA 2 August 1994; revised 25 October 1994; accepted 19 December 1994)