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MTO in "Clean" Oxidation of Thioether Fischer Carbene Complexes to Their Sulfoxides

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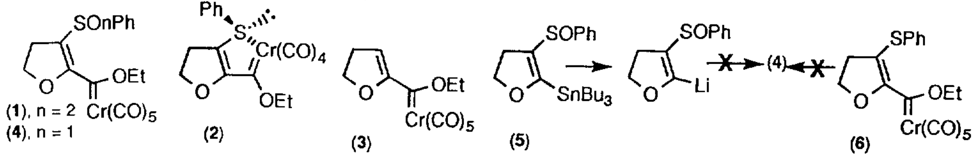
Abstract: Methyltrioxorhenium in conjunction with hydrogen peroxide provides a convenient method for the oxidation of thioether Fischer carbene complexes to their respective phenylsulfinyl complexes.

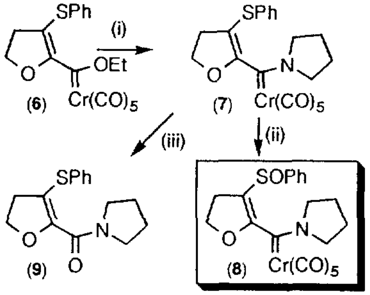
During the course of our recent investigations into the use of Fischer carbene complexes in organic synthesis[1] we have shown that the phenylsulfonyl complex (**1**) and the chelated thioether complex (**2**) provide a practical alternative to the parent carbene complex (**3**) in Dötz benzannulation reactions[2]. Further studies have naturally focused upon the preparation of the sulfinyl complex (**4**), which at the outset was deemed to be unstable with respect to oxidation at the metal centre. The preparation of sulfinyl and sulfonyl substituted transition metal complexes is an area of much current interest,[3] although there is only one other report[2,4] concerning the preparation of Fischer carbene complexes substituted in this manner. In this *Letter* we report our initial findings into the use of hydrogen peroxide in the presence of an activator (MTO) for the chemoselective oxidation of thioether - substituted Fischer carbene complexes.

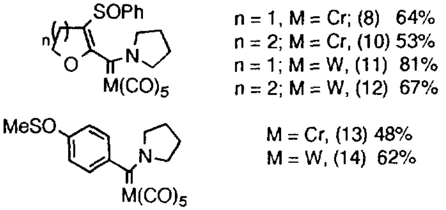


Scheme 1

Attempts to prepare the carbene complex (**4**) from (**5**) using the classical Fischer protocol[5] ((i) n-BuLi, THF, -78 °C; (ii) $Cr(CO)_6$, THF, -78 °C to 0 °C; (iii) Et_3OBF_4, H_2O) afforded a complex mixture of products. Likewise oxidation of the thioether complex (**6**) with oxidising agents such as MCPBA afforded intractable reaction mixtures, **Scheme 1**. Given that aminocarbene complexes have been observed to be more stable than the corresponding alkoxycarbene complexes,[6] oxidation of the pyrrolidino complex (**7**) was next attempted.

Exposure of the complex (**6**) to pyrrolidine (2 eq.; CH_2Cl_2; 20 °C) generated the pyrrolidino complex (**7**) as an air-stable, crystalline solid (mp. 103-105 °C) in 79% yield after column chromatography.[7] The current interest in developing "clean" oxidation procedures[8] led us to investigate the use of metal peroxo complexes in such oxidation reactions. Recent reports by Herrmann,[9] Espenson[10] and others[11] have demonstrated that catalytic methyltrioxorhenium (MTO) in the presence of stoichiometric hydrogen peroxide as reoxidant provides an efficient and robust procedure for the oxidation of a number of functional groups. Treatment of (**7**) with methyltrioxorhenium (MTO) (4 mol%) in the presence of hydrogen peroxide[11] (100 mol% of a 27.5 wt % soln.) in CH_2Cl_2-MeOH (1:1) at ambient temperature for five hours resulted in the isolation of the sulfinyl complex (**8**) in good yield (64%) as a flaky orange-red crystalline solid (mp. 106-108 °C). Blank experiments using hydrogen peroxide alone as the oxidising agent (1 eq. H_2O_2; MeOH-CH_2Cl_2 (1:1), 3 days, 20 °C) merely resulted in the formation of the amide (**9**) in 78% isolated yield, **Scheme 2**. The identity of the sulfinyl complex (**8**) was established upon the basis of spectroscopic techniques and finally by way of a single crystal X-ray analysis.[12] The isolation of (**8**) from (**7**) and its stability is remarkable given that dimethylsufoxide is a commonly used decomplexing agent for the conversion of aminocarbene complexes into amides.[13] Indeed, a blank experiment demonstrated that dissolution of the complex (**7**) in DMSO at 40 °C for 4 days resulted in the isolation of the amide (**9**) in 84% yield. Subsequent studies have demonstrated that the MTO oxidation protocol outlined above has general utility, enabling the preparation of the novel chromium and tungsten sulfinyl carbene complexes (**8**) and (**10**) to (**14**) from their respective thioether complexes in moderate - good isolated yields. The co - ordination chemistry and synthetic utility of these complexes is now under investigation.





Reagents: (i) pyrrolidine, 2 eq.; CH_2Cl_2; 20 °C; (ii) MTO, 4 mol%; H_2O_2; MeOH-CH_2Cl_2, 20 °C; (iii) H_2O_2; MeOH; 20 °C.

Scheme 2

Acknowledgements

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References and notes

1. King, J.; Quayle, P.; Malone, J. F. *Tetrahedron Letters*, **1990**, *31*, 5221; King, J. D.; Quayle, P. Tetrahedron Letters, **1991**, *32*, 7749; Beddoes, R. L.; King, J.; Quayle, P. *Tetrahedron Letters*, **1995**, *36*, 3027.
2. Painter, J. E.; Quayle, P.; Patel, P. *Tetrahedron Letters*, **1995**, *36*, 8089.
3. *e.g.* see Hachem, A.; Toupet, L.; Gree, R. *Tetrahedron Letters*, **1995**, *36*, 1849 and references therein.
4. Baldoli, C.; Buttero, P, D.; Licandro, E.; Maiorana, S.; Papagni, A. *Synlett*, **1995**, 666.
5. Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorganic Synthesis*, **1977**, *17*, 164.
6. Wang, S. L. B.; Su, J.; Wulff, W. D.; Hoogsteen, K. *J. Am. Chem. Soc.*, **1992**, *114*, 10665.
7. All new compounds were characterised by ^1H and ^{13}C nmr, ir, high resolution mass spectrometry and/or combustion microanalysis.
8. Sheldon, R. A. *Topics in Current Chemistry*, **1993**, *164*, 23.
9. Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, R. J.; Ramão, C. C. *Chem. Eur. J.* **1996**, 2, 168.
10. Hansen, P. J.; Espenson, *Inorg. Chem.*, **1995**, *34*, 5839.
11. Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Edn. Engl.*, **1996**, *35*, 533.
12. Beddoes, R. L.; Painter, J. E.; Quayle, P.; Patel, P. *Tetrahedron*, 1996, in preparation.
13. Wulff, W. D.; Anderson, B. A.; Toole, A. J. Xu, Y. *Inorganica Chimica Acta*, **1994**, *220*, 215.

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