Pergamon

Tetrahedron Letters 40 (1999) 489–490

TETRAHEDRON
LETTERS

A Dithioxo-bishydroxylaminomolybdenum Complex as Sulfur and Nitrogen transfer Reagent. Synthesis of Thioureas from Isonitriles

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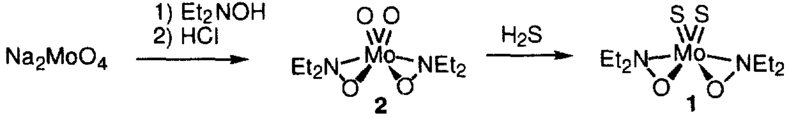
Received 6 October 1998; accepted 11 October 1998

Abstract: *Cis*-dithioxo-bis((*N,N*-diethyl)hydroxylamido(1-)-*O,N*)molydenum(VI) reacts with isonitriles to give the corresponding *N,N*-diethylthioureas. A mechanism is proposed for this S,N-transfer reaction.

Metal-oxo compounds are widely used in organic chemistry. They are commonly used in the oxidizing processes converting alkenes to epoxides and 1,2-diols.[1] No such chemistry has been developed from metal-thioxo compounds. This may be due, in part, to the relative scarcity of such compounds. However, both simple halide species such as $Cl_3Ta{=}S$, $Cl_3Nd{=}S$ and $Cl_3Mo{=}S$ have been reported[2] as well as some thioxo compounds with organic ligands such as porphyrins[3] or salen ligands.[4] Redox reactions involving such compounds have also been reported. *Berreau et al.*[3d] have described the sulfur atom transfer from a porphyrin tin-thioxo compound to a reduced form of molybdenum giving a molybdenum-thioxo complex, which, in turn can be reduced by triphenylphosphine to give molybdenum in its initial oxidation state. In light of these facts, and by analogy with the properties of metal-oxo compounds, we considered the possibility of sulfur atom transfer to organic substrates by a metal-thioxo complex.

Looking for stable, easily synthesized metal-thioxo derivatives, we were attracted by the Mo=S complex **1** described by Wieghardt *et al.* in 1982.[5] This compound is obtained in 2 steps from Na_2MoO_4 *via* the corresponding dioxo-compound **2**. It is a stable, violet, crystalline compound.



In order to test the possibility of transferring sulfur from this Mo=S complex to an organic substrate, we attempted the transformation of an isonitrile into an isothiocyanate.[6] Heating two equivalents of benzylisocyanide **3a** with complex **1** in chloroform at 60°C during a period of 6h led to a discoloration of the solution together with the appearance of a white precipitate.[7]

Examination of the ^1H and ^{13}C NMR spectra of the isolated product clearly showed that it was not the expected isothiocyanate **4a** but the thiourea **5a**. A similar result was obtain with cyclohexylisonitrile **3b**. It

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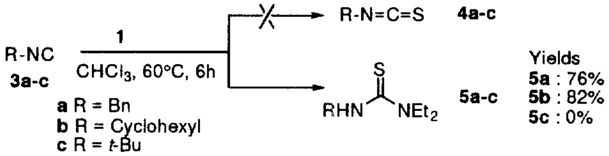
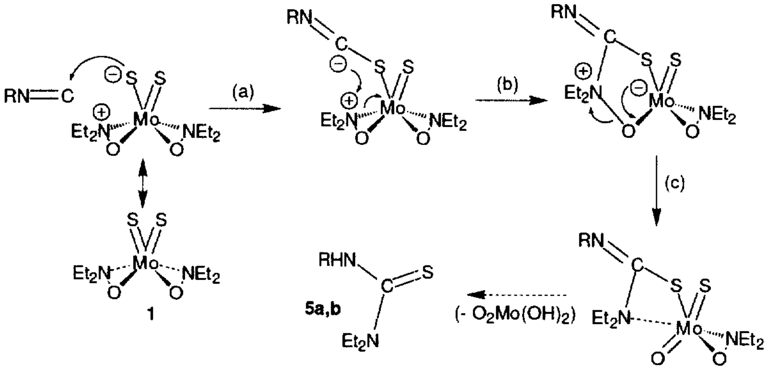
PII: S0040-4039(98)02418-6

should be noticed that the sterically crowded tertiary isonitrile **3c** did not give any reaction. Furthermore, when **3a** was reacted under similar conditions with the dioxo compound **2**, the isonitrile was recovered unchanged. No transformation into the corresponding isocyanate or urea was noticed.



The proposed mechanism for the attack of an isonitrile upon complex **1** is described in the following scheme. A nitrogen atom on the molybdenum can stabilize a positive charge in the zwiterionic resonance form bearing a negatively charged sulfur atom. The nucleophilic sulfur can attack the vacant orbital on the isonitrile carbon (step(a)). The resulting negatively charged carbon atom would react with the neighboring nitrogen atom (b), forming a five membered ring, and a rearrangement would lead to an oxo-thioxo metal complex (c); each molybdenum atom can react with two isonitriles and after attack by a molecule of water the thiourea is liberated. Steps (a) and (b) could be more or less concerted.



Future work concerns the trapping of the thiolate intermediate and the reactivity of **1** with other organic Lewis acids, to include a range of carbenes and electron poor alkenes.

References and notes

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7. Experimental procedure : Isonitrile **3a** (40mg, 0.34mmol) was added dropwise at room temperature to a solution of complex **1** (50mg, 0.15mmol) in $CHCl_3$ (1ml). The reaction mixture was then heated at 60°C for 6h. The solvent was evaporated and the obtained crude mixture was purified by thin layer chromatography (silica gel, eluant : $EtOAc/C_6H_{12}$: 1/3). The NMR spectra of the obtained thiourea (m= 51mg, yield from **1** : 76%) were in accordance with the literature : Hussein, A. Q.; Jochims, J. C. *Chem. Ber.*, **1979**, *112*, 1956-1972.