Reaction of a Molybdenum Hydrazido(2−) Complex with Silver Nitrate in Alcohols. Novel Variant of the Bamberger Reaction involving Concomitant *N*-Nitrosation

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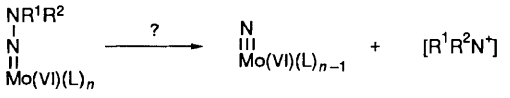
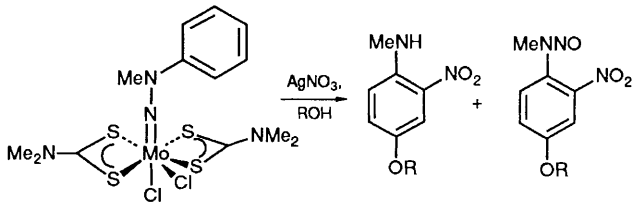
Treatment of dichlorobis(dimethyldithiocarbamato)[*N*-methyl-*N*-phenylhydrazido(2−)-*N'*]molybdenum(VI) with silver nitrate (3.3 equiv.) in alcoholic solvents results in cleavage of the hydrazido ligand from the metal to form *p*-alkoxyaniline derivatives.

Hydrazido(2−) complexes of molybdenum(II–IV) **1** ($R^1 = R^2 = H$) have attracted much attention as possible intermediates in models for the reaction mediated by the enzyme, nitrogenase, in which nitrogen is reduced to ammonia.[1] The reactions of the related molybdenum(VI) complexes bearing hydrazido ligands of more interest to the organic chemist, **1** ($R^1 = R^2$ = alkyl or aryl), in which N–N bond fission occurs (Scheme 1) have been largely ignored. In this report we detail the first of such reactions which results in the formation of *p*-alkoxyanilines analogous to those formed in the acid-mediated rearrangement of phenylhydroxylamines (the Bamberger rearrangement[2]).

Treatment of dichloro-bis(dimethyldithiocarbamato)[*N*-methyl-*N*-phenylhydrazido(2−)-*N'*]molybdenum(VI) **2**[3] with silver nitrate (3.3 equiv.) dissolved in methanol at room temperature for 15 h results in the formation of a grey-white precipitate (containing silver bis-dimethyldithiocarbamate by IR spectroscopy) and a solution containing two organic products derived from the reaction of the phenyl ring of the hydrazido ligand (Scheme 2). The major of these two products (30%) was 4-methoxy-2-nitro-*N*-methyl-aniline **3a** confirmed by synthesis of an authentic sample.[4] The minor product (14%) showed a very similar pattern in the ^1H NMR spectrum to that observed for the aniline **3a** except that the *N*-methyl signal and the doublet (9 Hz) for the aromatic proton *ortho* to the methylamino group had both been shifted downfield (by 0.4 and 0.55 ppm respectively). The absence of an NH in the IR spectrum of this product and the absence of coupling of the *N*-methyl with an adjacent NH, together with the above NMR shift, indicated that a group was attached to the amino nitrogen and that this group was electron-withdrawing. Mass

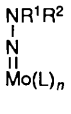


Scheme 1



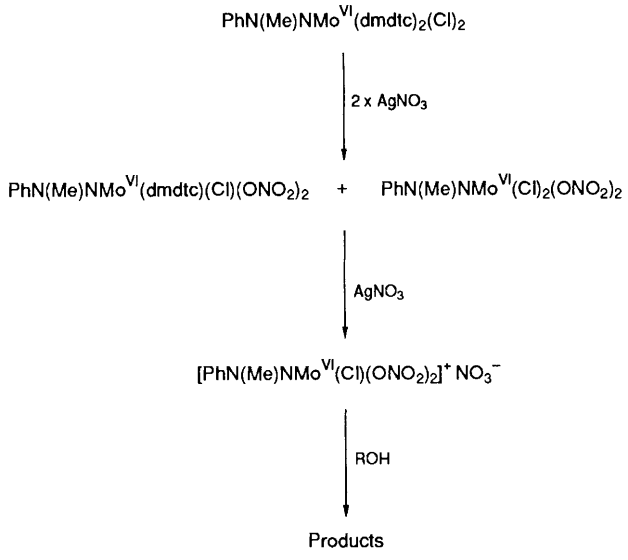
2 **3** **4**

a R = Me
b R = Et
c R = Pr^i



1

Scheme 2



dmdtc = dimethyldithiocarbamato

Scheme 3

spectrometry pointed to nitroso for this group and this was confirmed by *N*-nitrosation[5] of the aniline **3a** to give the nitrosoaniline **4a** identical in all respects with the minor product.

The same cleavage reaction proceeds from the dibromo congener of complex **2** to give aniline **3a** exclusively but in lower yield (14%).

That formation of the *N*-nitroso compound represents a major decomposition pathway for complex **2** is indicated by the following: (*i*) under reflux conditions in methanol the only organic product isolable was *N*-methyl-*N*-nitrosoaniline (12%); (*ii*) in ethanol at room temperature, the nitrosoaniline **4b** is the sole product (27%) whereas in propan-2-ol both the isopropoxy analogue **4c** (5%) and *N*-methyl-*N*-nitrosoaniline (6%) are formed.

We believe that the first step in this transformation is the stripping of one or both of the dithiocarbamato ligands from the metal and their replacement by nitrato (Scheme 3). The third equivalent then removes a chloride or a dithiocarbamate to give a cationic complex in which N–N bond cleavage is enhanced. Either a free phenyl-stabilised nitrenium ion is released (as in the Bamberger rearrangement[2]), which is then attacked by the alcohol in the *para*-position or the cationic complex is directly attacked in the same fashion. Ring nitration could be mediated by the nitric acid released in this step. The mechanism of the nitrosation process and the timing of the nitration and nitrosation steps are unknown.

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