Investigation of the Potential of Molybdenum(VI) Hydrazido(2—) Complexes as Sources of Nitrenium Ions: Cleavage of the N–N Bond and Incorporation of the β-Nitrogen Group into Solvent Molecules

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Photolysis or thermolysis of bis(*N*,*N*-dimethyldithiocarbamato)bis[*N*-alkyl-*N*-phenylhydrazido(2−)]-molybdenum(VI) complexes in 1,1,2,2-tetrachloroethane results predominantly in transfer of the hydrazido group to the solvent with formation of dichloroacetohydrazides. A small amount of the corresponding dichloroacetamides are produced by N–N cleavage and N(R)Ph transfer. In contrast, the latter process dominates the reaction of dichlorobis(*N*,*N*-dimethyldithiocarbamato)mono-[*N*-alkyl-*N*-phenylhydrazido(2−)]molybdenum(VI) complexes with silver nitrate in alcohols occuring concomitantly with ring methoxylation and nitration and *N*-nitrosation. Neither transfer of N(R)Ph appears to involve free nitrenium ions.

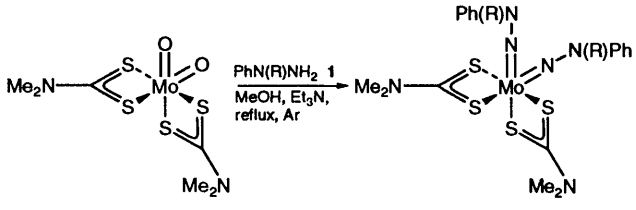
Nitrenium ions are ephemeral species whose intermediacy has often been invoked in the reactions of *N*-chloroamines [R_2NCl ($+Ag^+$)],[1] hydroxylamines [R_2NOH ($+H^+$)][2] and their derivatives [(R_2NOSO_2R),[3] ($R_2NOCOAr$)[4]], and alkyl azides [RN_3 (+alkylating agents),[5] ($+H^+$)[6]]. Only sparingly have hydrazines [R_2NNH_2 (+AmONO)][7] or related derivatives (1-anilino-2-methyl-4,6-diphenylpyridinium salts)[8] been investigated as possible precursors to nitrenium ions.

Considerable debate has arisen over whether free nitrenium ions are formed under the conditions described in many of these studies or whether concerted reactions in which the nitrogen atom develops partial electron deficiency represent the true picture. These mechanistic arguments notwithstanding, the fact remains that the readily available hydrazines have contributed little to this area of chemistry. The two examples mentioned above for the conversion of hydrazines into products of nitrenium ion derivation illustrate the need to have one nitrogen of the hydrazine become part of a leaving group. The possibility of achieving this end by complexation of the β-nitrogen of a 1,1-disubstituted hydrazine with a powerfully electron-withdrawing metal seemed worthy of consideration, especially since the product of the desired N–N bond cleavage on the metal side could be a metal nitrido complex whose stability[9] might add thermodynamic impetus to the reaction. Molybdenum was chosen as the activator because of the ready availability of hydrazido(2−) complexes with this metal in its highest oxidation state(VI).

This report, therefore, details our attempts to effect nitrenium like reactions using molybdenum hydrazido(2−) complexes. Some of this work has been communicated earlier.[10]

Results and Discussion

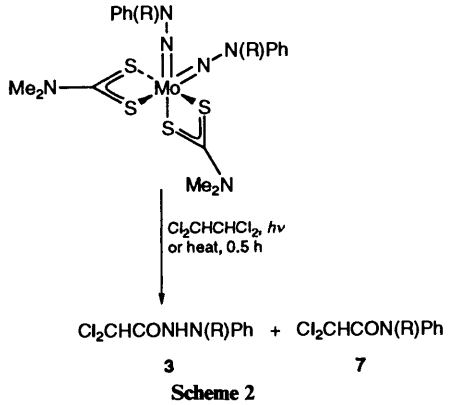
N-Alkyl-*N*-phenylhydrazines **1** have been synthesized previously by the phase-transfer catalysed *N*-alkylation of benzaldehyde phenylhydrazone followed by acid hydrolysis.[11] We found that the alkylation step in this sequence worked admirably but we could not hydrolyse the resultant hydrazones under a range of conditions including those reported by the authors. We, therefore, resorted to the simple phase-transfer catalysed monoalkylation of phenylhydrazine itself which worked regiospecifically in most cases probably because of the activating influence of the phenyl group on the adjacent NH. Condensation of these hydrazines with bis(*N*,*N*-dimethyldithiocarbamato)dioxomolybdenum(VI) according to the procedure



Scheme 1 All = $CH_2CH{=}CH_2$; Pg = $CH_2C{\equiv}CH$

of Dilworth and Zubieta[12] provided the starting bis-hydrazido complexes **2** (Scheme 1).[13]

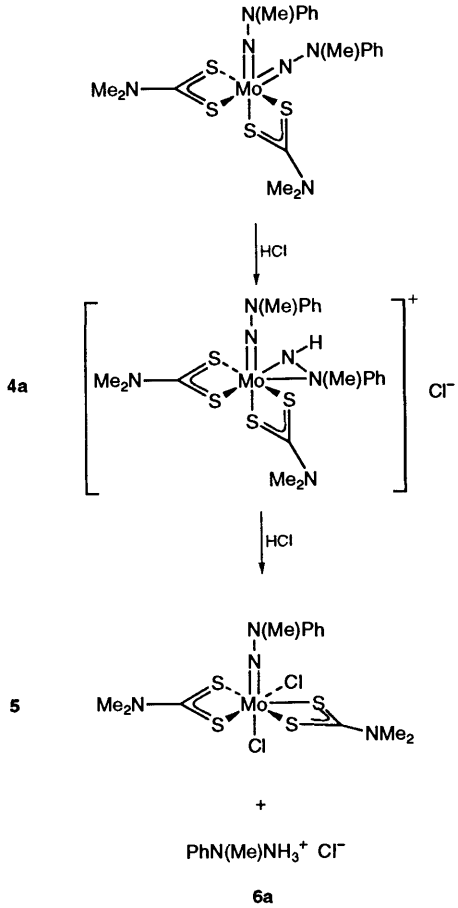
Thermolysis and Photolysis of Complexes **2**.—Representative complex **2a** proved to be very stable to both heat (in boiling anisole or toluene) and light in a wide range of solvents. The exceptions were carbon tetrachloride, in which decomposition to a number of unidentifiable products occurred, and 1,1,2,2-tetrachloroethane (TCE). The last solvent was unique in causing a dramatic colour change on dissolution of the complexes from yellow–orange to blood-red, **2a–f**, or purple, **2g**. Irradiation of such solutions under argon in a Pyrex immersion-well reactor (λ = 300 nm) at 15 °C by means of an Hanovia 125W medium-pressure mercury arc lamp for 0.5 h led to the formation of *N*-alkyl-*N*-phenyldichloroacetohydrazides **3** in moderate yields (Scheme 2), identified by comparison of their spectral data with authentic samples prepared by the reaction of



Scheme 2

dichloroacetyl chloride with the parent hydrazines. By-products were formed in the cases of **2d** (*N*-benzylaniline, 20%) and **2g** (diphenylamine, 28%; *N*,*N*-diphenylhydrazine, 30%) only. The reaction can also be done thermally. Thus, leaving a mixture of **2a** in acidic TCE in the dark at 30 °C for 0.5 h gave a 90% yield of **3a**.

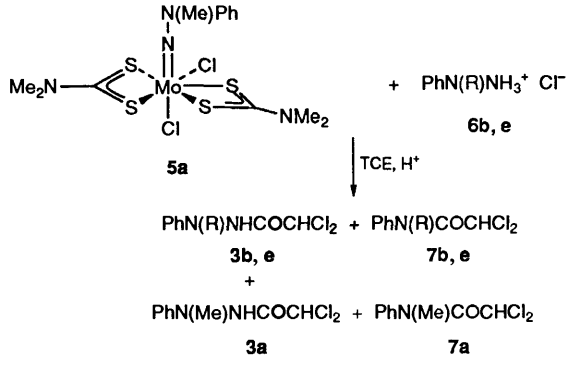
We wondered what factor was unique to TCE which made it so reactive towards the complexes compared to other solvents (in CCl_4 decomposition was much slower). It was quickly discovered that TCE contains substantial amounts of HCl even after distillation. When the complexes were dissolved in TCE which had been washed with aqueous sodium hydrogencarbonate and water (to neutrality) just prior to use, they neither changed colour not underwent photochemical cleavage to **3**. This experiment established that HCl was a necessary component for reaction. Dilworth, Zubieta and their colleagues had previously shown that HCl converted **2a** through the seven-coordinate η^2-hydrazido(1−)-hydrazido(2−) intermediate **4a** into the dichloromonohydrazido(2−) complex **5a** and *N*-methyl-*N*-phenylhydrazine hydrochloride **6a** (Scheme 3).[14]



Scheme 3

Thus, **4**, **5** and **6** became possible candidates for the photolabile species responsible for the formation of **3**. Photolysis of **4a** (X = Cl or BPh_4), **5a**, **6a** or a combination of **5a** and **6a** in neutralised TCE failed to provide any hydrazide or amide. Likewise, in acidic TCE neither **5a** nor **6a** separately reacted (**4a** cannot be photolysed in acidic TCE because it undergoes rapid conversion into **5a** and **6a** on dissolving in this solvent). However, **5a** and **6a** in combination in acidic TCE gave an unexpected result. Although the hydrazide **3a** was obtained, it was admixed (1:1) with the corresponding amide **7a** (identified by spiking an NMR sample of the mixture with a small quantity of authentic material) in total 60% yield. This was the first observation of the desired N–N cleavage in substantial amounts [amide **7a** had previously been seen in low yields when the photolysis of **2a** was carried out in a quartz apparatus using a copper sulfate filter ($\lambda > 280$ nm)].

The simultaneous involvement of both **5a** and **6a** suggested a crossover experiment. When complex **5a** was treated with acidic TCE at 30 °C in the dark in the presence of *N*-ethyl-*N*-phenylhydrazine hydrochloride **6b** the organic product mixture consisted of *N*-methyl amide **7a**, *N*-methyl hydrazide **3a** and *N*-ethyl amide **7b** and *N*-ethyl hydrazide **3b** by ^{1}H NMR spectroscopy. Likewise a mixture of **5a** and **6e** generated all four possible products (Scheme 4).

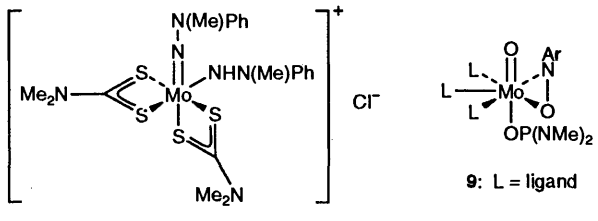


Scheme 4 R = Et (**b**), $CH_2CH{=}CH_2$ (**e**)

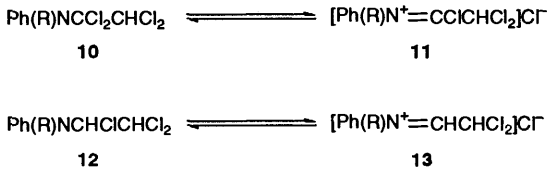
These results showed that an equilibrium exists between the photoactive species and the dichloro complexes **5** plus the hydrazine hydrochlorides **6**. This points to an intermediate complex between **2** and **5** as the species which reacts with TCE to produce the N–N cleavage product, the amide **7**. The simplest role for the HCl is to mediate the formation of this complex but it is also possible that it activates it as well [recently, it has been shown that a peroxo complex of copper needs to undergo protonolysis to a hydroperoxo complex before it is capable of transferring oxygen to substrate: [eqn. (1)].[15]

$$L_nCu\cdots O_2\cdots CuL_n + H^+ \longrightarrow L_nCu\cdots OOH\cdots CuL_n + PPh_3 \longrightarrow OPPh_3 \quad (1)$$

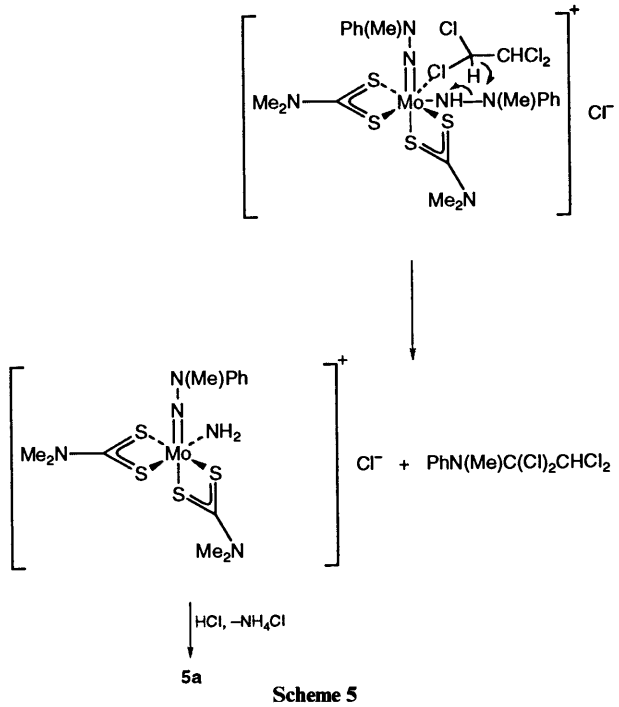
The nature of this intermediate remains unknown although the choice is limited and the complex **4** or the equivalent η'-species **8** are likely candidates; **4** resembles the η^2-nitroso complexes **9**



shown by Mares[16] and by Sharpless[17] to act as agents for transfer of NAr possibly by a mechanism involving nitrenes. We assume that the amides **7** derive by hydrolysis of their respective α,α-dichloro amines/α-chloro iminium salts **10**/**11** since these are known to react violently with water[18] and no attempt was made to dry the TCE thoroughly in our experiments. In our

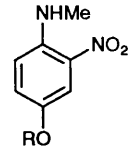


case, the mechanism of the transfer of N(R)Ar to TCE to give **10/11** is unknown although the lack of products of attack of nucleophiles on the aromatic ring probably precludes the involvement of the free nitrenium ion $^{+}$N(R)Ar in their formation.[6] The free-radical, $^{\bullet}$N(R)Ar, and the anion, $^{-}$N(R)Ar, seem similarly unsuited to the production of **10/11** since both should either produce Ar(R)NH by hydrogen and proton abstraction of the α-chloro amine/iminium salt **12/13** by homolytic and heterolytic displacement, respectively. We currently favour protonation–displacement occurring in the ligand sphere of the metal (Scheme 5). The sole inorganic product identified from the reaction was the dichloro complex **5a**.

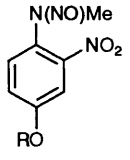


Scheme 5

Reaction of Dichloro Complexes **5** *with Silver Nitrate.*—It was apparent that any chance of observing products derived from nitrenium ions in the decomposition of hydrazido complexes would require the metal to be even more electron-withdrawing than heretofore. Cationic molybdenum(VI) complexes seemed to fit the requirement and chloride abstraction from the dichloro complexes **5** offered a route to such species. Reaction of **5a** with silver nitrate (3.3 equiv.) in methanol at room temperature overnight (15 h) under argon gave a grey–white precipitate of mixed silver salts [containing silver bis(dimethyldithiocarbamate) by comparison of its IR spectrum with that of an authentic sample] and two organic products free of molybdenum in the supernatant. After chromatography on SiO_2, the less-polar material (30% yield) was eluted as a red solid, m.p. 96–98 °C, which was clearly characterised as a trisubstituted benzene by ^{1}H NMR spectroscopy. Moreover, the three 1 H peaks at 6.83 (doublet, 9 Hz, *ortho*-coupling), 7.19 (double doublet, 9 and 4.3 Hz, *ortho*- and *meta*-coupling) and 7.62 ppm (doublet, 4.3 Hz, *meta*-coupling) established a 1,2,4-substitution pattern on the aromatic ring. That two of the substituents were NHMe and OMe was indicated by a doublet and a singlet at 3.0 and 3.8 ppm, respectively, together with a broad band at 8.0 ppm (NH). The furthest downfield of the aromatic protons was at a chemical shift value suggestive of an electron-withdrawing group for the last substituent. This was confirmed as nitro by mass spectrometer ($M^+ - 46$) and IR spectroscopy (1522 and 1350 cm^{-1}). The loss of 17 (OH) mass units in the mass spectrum indicated that the nitro group was *ortho* to the amino group.[19] Of the two possible methoxy derivatives of 2-nitro-*N*-methylaniline with a 1,2,4-substitution pattern the 4-MeO isomer was reported to be a red solid, m.p. 98–100 °C,[20] whereas the 5-MeO compound was not well defined.[21] The latter was, therefore, synthesized from 5-methoxy-2-nitroacetanilide[22] by *N*-methylation and deacetylation according to the method of Wilshire[20] and obtained as an ochre-coloured solid, m.p. 93–96 °C. In its ^{1}H NMR spectrum the *ortho*-coupled doublet was upfield (6.45 ppm) of that for the 4-MeO isomer and the *meta*-coupled doublet was upfield of the double doublet (at 7.6 and 7.9 ppm, respectively) the reverse of the situation for its isomer. Clearly, the first eluted product of the silver nitrate reaction was indicated to be 4-methoxy-2-nitro-*N*-methylaniline **14a** confirmed by a mixed m.p. with an authentic sample of this compound.



14a R = Me
b R = Et
c R = Pr^i



15a R = Me
b R = Et
c R = Pr^i

The more-polar organic product from the SiO_2 column was an orange gum obtained in 14% yield. It showed a very similar pattern in its ^{1}H NMR spectrum to that for the aniline **14a** 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 shifts, indicated that a group was attached to the amino nitrogen and that this group was electron-withdrawing. Mass spectrometry pointed to nitroso for this group ($M^+ - 30$) and this was confirmed by *N*-nitrosation[23] of the authentic sample of the aniline **14a** to give the nitrosoaniline **15a** identical in all respects with the more-polar product from the silver nitrate reaction.

The molybdenum-containing products from this reaction were not fully characterised but showed strong bands in the IR spectrum at 949 and 1048 cm^{-1} a region where both Mo=O and MoN groups absorb.[24]

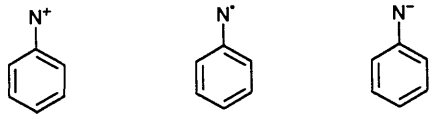
Reaction of the dibromo congener of complex **5a** produced only the aniline **14a**. In contrast, reaction of **5a** in ethanol or isopropyl alcohol favoured the nitrosoanilines **15b** (27%) and **15c** (5%) with only traces of the corresponding anilines **14b, c** being detected in the crude reaction mixtures. Heat was deleterious to the production of **14** or **15** since a reaction under reflux in methanol produced only *N*-methyl-*N*-nitrosoaniline (12%) [also a side-product (6%) of the reaction in isopropyl alcohol].

The formation of all these products from **5** requires a number of steps, namely, removal of chloride and dithiocarbamate from the molybdenum complex by silver, N–N cleavage, methoxylation of the aromatic ring, nitration of the aromatic ring, and *N*-nitrosation. Some of these steps may be concerted.

We assume that the first step is the stripping of the ligands from the metal giving one or more nitrato complexes. The mass balance of silver salts precipitated in the reaction shows that both dithiocarbamate and one chloride are removed leaving one chloride attached to the metal. Since little is known about nitrato-molybdenum(VI) complexes except that $MoO_2(NO_3)_2$ is air- and moisture-unstable,[25] we did not know if the resultant complexes were robust enough to await the next step or whether N–N cleavage occurred simultaneously with ligand removal. In this context, it is interesting to note that reaction of complex **2a** with copper(II) acetate, trifluoroacetate or acetylacetonate

results in the production of copper bis(dimethylaminodithiocarbamate) and a number of organic products (including *N*-methylaniline and *N*-methyl-*N*-phenylhydrazine) derived from the hydrazido ligand; these results point to the instability of molybdenum hydrazido complexes in the absence of dithiocarbamato ligands whether or not they contained nitrato ligands.

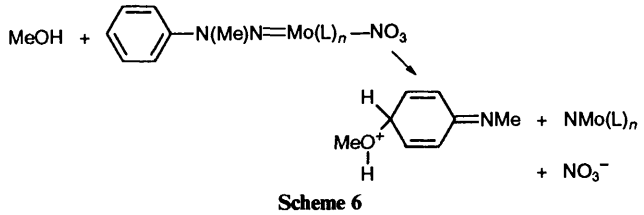
Moving on to the next step, if N–N cleavage occurs separately it can produce a nitrenium ion **A**, an aminyl radical **B**, or an amide anion **C** which could suffer nucleophilic attack, hydrogen abstraction or electrophilic attack, respectively. Ring-unsubstituted products may derive from either **B** or **C** but the products bearing *p*-MeO can only arise through the intermediacy of **A**; in this, the formation of methoxylated products resembles the reaction of *N*-phenylhydroxylamines with acid in alcoholic solvents (the Bamberger rearrangement) to give *p*-alkoxyanilines which is proposed to proceed through **A**.[26] However,



A **B** **C**

attempts to trap free **A** by carrying out the reaction in the presence of various olefins or aromatics failed; these experiments uniformly produced *N*-methyl-*N*-nitrosoaniline as the only identifiable organic product (15–30% yields from reactions in the presence of anisole, cycloocta-1,5-diene, cyclohexene, allyl acetate, and *trans*-stilbene; furan, cyclopentadiene, norbornene and methyl acrylate failed to give any identifiable products). In addition, the dependence of the yield of *p*-alkoxy products on the size of the alcohol suggests that a free nitrenium ion **A** is not produced since this would be expected to be indiscriminate in its attack; indeed, Bamberger reports that methoxy and ethoxy derivatives were formed with comparable ease.[27] We, therefore, favour attack of the alcohol on a molybdenum complex.

The stoichiometry of methoxylation by concerted attack on a nitrato-molybdenum complex necessarily produces nitric acid as a by-product which would provide the necessary agent for nitration of the ring (it should be noted that methoxylation does not occur without concomitant nitration) (Scheme 6). Indeed, in the presence of bases (excess of pyridine or 5 equiv. of either NaOAc or NaOMe) both nitration and methoxylation were eliminated.



Scheme 6

The most intriguing step is nitrosation for it implies the deoxygenation of nitrate [in the presence of 5 equiv. of either NaOAc or NaOMe the only identifiable product is *N*-methyl-*N*-nitrosoaniline (10%) which suggests that deoxygenation occurs on the nitrate anion rather than nitric acid]. It is also the dominant organic reaction in the sense that it occurs under a much wider range of conditions than nitration or methoxylation.

None of the above attempts to trap **A** with olefins gave any clue to the nature of the nitrosating agent. However, when the reaction was carried out in the presence of styrene an 82% yield of a crude, orange oil was obtained. This oil could not be purified by SiO_2 chromatography without substantial loss of material and, therefore, a tentative assignment of structure was made on the basis of the spectral characteristics of the crude material. The most informative of the spectroscopic techniques was ^{13}C NMR which showed that the major component of this crude product had a CH_2 attached to a heteroatom group (DEPT 135 spectrum, 68 ppm), one phenyl quaternary and one quaternary sp^2-carbon (DEPT 135 spectrum, 133 and 148.5 ppm, respectively) and phenyl CH carbons (DEPT 90 spectrum, 126, 129 and 130 ppm). This was consistent with an eight-carbon skeleton, $PhC(=X)CH_2Y$, probably derived from styrene. The chemical shift value (148.5 ppm) of the non-aromatic quaternary carbon was indicative of an oxime (X = NOH) and the presence of this group was supported by the appearance of an OH group in the IR (3310 cm^{-1}) and ^1H NMR (broad signal at 9.2 ppm) spectra. Bands at 1565vs and 1340s cm^{-1} in the IR spectrum pointed to NO_2 for Y, consistent with a molecular ion at *m/z* 180 and a peak at $M^+ - 46$ in the mass spectrum. Thus, the compound was indicated to be α-nitroacetophenone oxime, and our IR and ^1H NMR spectra agree with those reported in the literature.[28] This is a known product of the reaction of styrene with N_2O_3[29] or HNO_2[30] and suggests that one or other of these reagents is responsible for the *N*-nitrosation in our reaction.

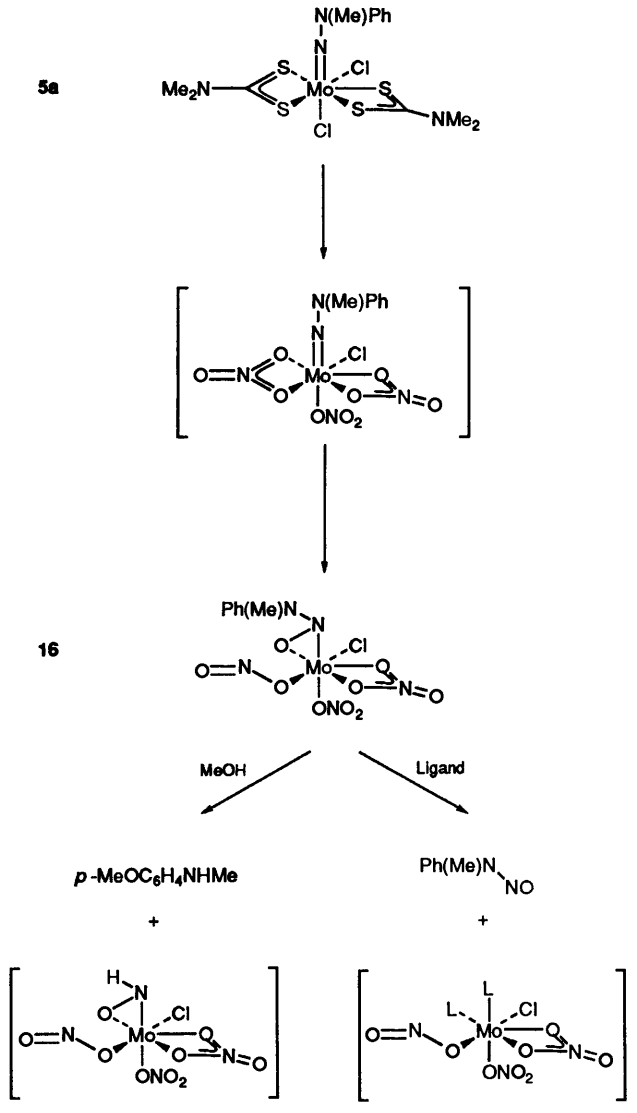
Many studies have shown that molybdenum(V) complexes will reduce nitrate to nitrogen dioxide[31] and nitrogen dioxide to nitrous oxide[32] but it is difficult to envisage the formation of molybdenum(V) complexes in our system (*m*-dinitrobenzene has no effect on the reaction implying the absence of any radical chain processes and neither methyl acrylate nor styrene is polymerised under the reaction conditions indicating that a non-chain radical process is not likely). Molybdenum(IV) has been implicated in the reduction of nitrate to nitrite[33] but the formation of molybdenum(IV) requires a reductive elimination from an intermediate molybdenum(VI) species. Reductive elimination of combinations of nitrato, chloride and hydrazido ligands seems inconceivable since such processes would result in the formation of kinetically reactive species, *e.g.* $ClONO_2$ which would themselves be prone to oxidatively add back onto molybdenum(IV).

An alternative to reductive elimination is the redox reorganisation of the hydrazido ligand and an adjacent nitrato to give a η^2-nitrosoaniline–nitrite complex **16**. This complex could suffer two fates (Scheme 7). In one, *para*-attack by alcohol with concomitant N–N cleavage occurs as for the hydrazido complex above. In the second, simple ligand replacement provides the ubiquitous *N*-methyl-*N*-nitrosoaniline. An advantage of invoking this second step is that it obviates the need to consider *N*-methylaniline as a precursor to *N*-methyl-*N*-nitroaniline; the formation of *N*-methylaniline and 4-alkoxy-2-nitro-*N*-methylaniline, **14**, in the same reaction requires that N–N cleavage proceed simultaneously with and without alkoxylation, an unlikely event. Complex **16** could also suffer methanolysis to give the nitrous acid required for the formation of nitrosoanilines **15** and α-nitroacetophenone oxime.

In conclusion, it has been demonstrated that molybdenym(VI) hydrazido(2−) complexes are able to transfer PhNR to solvent molecules. Despite the formation of products which are formally derived from nitrenium ions, the evidence suggests that these species are not involved as free entities. In some cases (amide formation from TCE, production of *N*-methyl-*N*-nitrosoaniline from **5**) reduction of the bond order between molybdenum and the α-nitrogen atom of the hydrazido(2−) ligand appears necessary for N–N cleavage and negates our assumption that a nitrido complex is the ultimate inorganic product of all such processes.

Experimental

Melting points were determined on a Kofler hot-stage or Gallenkamp apparatus with benzoic acid as reference. IR



Scheme 7

spectra were recorded on Perkin-Elmer 1720 FT or Perkin-Elmer 881 grating spectrometers as thin films or Nujol mulls. ^1H and ^{13}C NMR spectra were run on JEOL FX 90Q, Bruker WM-250, JEOL GSX 270 or Bruker AM-500 machines using $CHCl_3$ or tetramethylsilane as standards in $CDCl_3$ unless otherwise specified; coupling constants, *J*, are recorded in Hz. Mass spectra were recorded on a Micromass 7070B instrument by EI or FAB (*m*-nitrobenzyl alcohol matrix).

Column chromatography was performed on Crosfield Sorbsil C-60-40/60 silica gel under gravity or low positive pressure. LP refers to redistilled light petroleum, b.p. 40–60 °C; ether refers to diethyl ether. Ether and tetrahydrofuran were distilled from sodium wire/benzophenone and molten potassium, respectively, under argon immediately prior to use. Dichloromethane, acetonitrile and toluene were distilled from phosphorus pentoxide, calcium hydride and sodium wire, respectively, under argon just prior to use. 1,1,2,2-Tetrachloroethane was purified in the following way: a batch (400 cm^3) was boiled with concentrated sulfuric acid (3 × 15 cm^3) and then washed with water (3 × 15 cm^3), dried briefly ($CaCl_2$), distilled (b.p. 147–149 °C at 760 mmHg) and stored in the dark. All other solvents and reagent were purified by standard methods.

Bis(dithiocarbamato)bis[hydrazido(2−)] complexes of molybdenum(VI)[12,13] and dichlorobis(dithiocarbamato)mono-[hydrazido(2−)] complexes of molybdenum(VI)[14,34] were prepared according to the literature.

N-Methyl-*N*-phenylhydrazine, **1a**, and *N*,*N*-diphenylhydrazine (as its hydrochloride), **1g**, were purchased from the Aldrich Chemical Company.

Phase Transfer-catalysed Alkylation of Phenylhydrazine.—Phenylhydrazine (1.0 g, 9.3 mmol) was added to a stirred solution of aqueous sodium hydroxide (12.5 mol dm^{-3}; 10 cm^3) containing tetrabutylammonium chloride (0.13 g, 0.47 mmol, 5 mol%) and the alkylating agent (1.1 equiv.) was then added. The fine emulsion was stirred vigorously under conditions dependent on the alkylating agent and then diluted with water (30 cm^3). The mixture was extracted with chloroform (3 × 10 cm^3), and the combined extracts were dried and evaporated to give the crude product which was purified by distillation.

N-Ethyl-*N*-phenylhydrazine **1b**, from ethyl iodide (15 h, 25 °C), b.p. 55 °C at 0.15 mmHg (lit.,[35] 115–119 °C at 20 mmHg) (32%). *N*-Propyl-*N*-phenylhydrazine **1c**, from propyl iodide (15 h, 25 °C), b.p. 74 °C at 0.4 mmHg (lit.,[35] 122–130 °C at 20 mmHg) (40%). *N*-Benzyl-*N*-phenylhydrazine **1d**, from benzyl chloride (0.5 h, 60 °C), b.p. 120 °C at 0.15 mmHg (lit.,[35] 157–159 °C at 4 mmHg) (71%). *N*-Allyl-*N*-phenylhydrazine **1e**, from 3-bromopropene (0.5 h, 60 °C), b.p. 50 °C at 0.2 mmHg (lit.,[36] 177 °C at 110 mmHg) (70%). *N*-Prop-2-ynyl-*N*-phenylhydrazine **1f**, from 3-chloropropyne (15 h, 25 °C), b.p. 60 °C at 0.2 mmHg (lit.,[11] 135 °C at 6 mmHg) (32%).

Photolysis of Bis(dithiocarbamato)bis[hydrazido(2−)] Complexes of Molybdenum(VI) in TCE.—Complex **2** (0.17 mmol) was dissolved in TCE (30 cm^3) to afford a blood-red solution (purple in the case of **2g**) which was degassed with argon for 40 min in a Pyrex immersion-well photochemical reactor. The mixture was photolysed for 0.5 h (3 h for **2g**) under an atmosphere of argon at 15 °C by means of a Hanovia 125W medium-pressure mercury-arc lamp. The resultant, dark-brown solution was concentrated on a rotary evaporator and the crude material was applied to a column of silica gel. Elution with ether–LP provided the products as follows (the major rotamer of the hydrazides is designated rotamer A in all cases).

N-Methyl-N-phenyldichloroacetohydrazide **3a**, a white solid, m.p. 93–95 °C (21 mg, 52%); ν_{max}/cm^{-1} 3386 (NH), 1656 (CO), 1598 (C=C); δ_H(270 MHz) 3.2 (3 H, 2 × s, NMe), 6.0 (1 H, s, CCl_2H of rotamer A), 6.5 (1 H, s, CCl_2H of rotamer B), 6.8–7.0 (3 H, m, NPh *m*- and *p*-H), 7.3–7.4 (2 H, m, NPh *o*-H) and 8.4 (1 H, br s, NH) (ratio of rotamers is 2.5:1); *m*/*z* 234 and 232 [10 and 16% respectively (Found: M^+, 232.0165. $C_9H_{10}Cl_2N_2O$ requires 232.0170)], 121 (100%, PhMeNNH), 105 (15%, PhMeN − H) and 77 (20%, Ph); an authentic sample was prepared from the reaction of dichloroacetyl chloride and the parent hydrazine (Found: C, 46.7; H, 4.3; N, 11.8. $C_9H_{10}Cl_2N_2O$ requires C, 46.38; H, 4.32; N, 12.02%); δ_C(68 MHz) 41 (NMe in rotamer A), 44 (NMe in rotamer B), 63 ($CHCl_2$ in B), 66 ($CHCl_2$ in A), 114 (A), 115 (B), 121 (A), 123 (B), 130 (both rotamers), 149 (A), 150 (B), 160 (CO in A) and 161 (CO in B); obtained as a 3:1 ratio of rotamers.

Photolysis of **2a** under the above conditions but in a quartz apparatus with a 0.034 mol dm^{-3} aqueous copper sulfate stabilised with sulfuric acid, gave *N-methyl-N-phenyldichloroacetamide* **7a** as a 1:1 mixture with the hydrazide **3a** in combined 38% yield. An authentic sample of the amide was prepared by the reaction of dichloroacetyl chloride and *N*-methylaniline as a white solid, m.p. 69–71 °C (Found: C, 49.6; H, 4.0; N, 6.3. $C_9H_9Cl_2NO$ requires C, 49.57; H, 4.16; N, 6.42%); ν_{max}/cm^{-1} 1688 (CO) and 1461; δ_H(270 MHz) 3.3 (3 H, s, NMe), 5.85 (1 H, s, $CHCl_2$), 7.25 (2 H, m, NP, *m*-H) and 7.4–7.5 (3 H, m, NPh, *o*- and *p*-H); δ_C(68 MHz) 39 (NMe), 64 ($CHCl_2$), 127.5, 129.5, 131, 142 and 164 (CO); *m*/*z* 219 and 217 (18% and 28% respectively, M^+), 134 [100%, PhN(Me)CO], 106 (42%, PhNMe) and 77 (58%, Ph).

N-*Ethyl*-N-*phenyldichloroacetohydrazide*, **3b**, an off-white solid, m.p. 79–81 °C (20 mg, 49%); ν_{max}/cm^{-1} 3229 (NH), 1695 (CO), 1601 and 1498; δ_H(90 MHz) 1.2 (3 H, t, Me), 3.6 (2 H, q, CH_2), 6.0 (1 H, s, $CHCl_2$ in rotamer A), 6.55 (1 H, s, $CHCl_2$ in rotamer B), 6.8–7.1 (3 H, m, NPh *m*- and *p*-H), 7.2–7.4 (2 H, m, NPh *o*-H) and 8.0 (1 H, br s, NH) (ratio of rotamers is 3.5:1); δ_C(125 MHz) 10 (Me in rotamer B), 11.5 (Me in rotamer A), 47 (NCH_2 in A), 50 (NCH_2 in B), 62 ($CHCl_2$ in B), 65 ($CHCl_2$ in A), 114 (A), 115 (B), 120 (A), 122 (B), 130 (both rotamers), 147 (both rotamers), 163 (CO in A), 168 (CO in B); *m*/*z* 248 and 246 (10 and 15% respectively, M^+), 149 (13%), 135 (100%, PhEtNNH), 119 (42%, PhEtN – H), 107 (45%) and 77 (67%, Ph); an authentic sample was prepared by reaction of dichloroacetyl chloride with the parent hydrazine (Found: C, 48.65; H, 4.7; N, 11.3. $C_{10}H_{12}Cl_2N_2O$ requires C, 48.60; H, 4.89; N, 11.33%).

N-*Phenyl*-N-*propyldichloroacetohydrazide*, **3c**, an off-white solid, m.p. 119–121 °C (16.5 mg, 40%); ν_{max}/cm^{-1} 3220 (NH), 1691 (CO), 1601 and 1498 cm^{-1}; δ_H(270 MHz) 1.0 (3 H, t, Me), 1.6–1.8 (2 H, m, CH_2), 3.5 (2 H, t, CH_2N), 6.0 (1 H, s, $CHCl_2$ in rotamer A), 6.5 (1 H, s, $CHCl_2$ in rotamer B), 6.8–7.0 (3 H, m, NPh *m*- and *p*-H), 7.3 (2 H, m, NPh *o*-H) and 8.0 (1 H, br s, NH) (ratio of rotamers is 3.4:1); δ_C(125 MHz) 11 (Me, both rotamers), 18 (CH_2, rotamer B), 20 (CH_2, rotamer A), 54 (CH_2N, A), 57 (CH_2N, B), 62 ($CHCl_2$, B), 65 ($CHCl_2$, A), 114 (A), 115 (B), 120 (A), 122 (B), 129 (both rotamers), 148 (both rotamers), 157 (B) and 163 (A); *m*/*z* 262 and 260 (48 and 74%, respectively, M^+), 233 and 231 (25 and 38%, respectively, $M^+ - Et$), 149 (100%, PhPrNNH), 133 (88%, PhPrN – H), 121 (21%) and 104 (39%); an authentic sample was prepared by reaction of dichloroacetyl chloride with the parent hydrazine (Found: C, 50.5; H, 5.4; N, 10.6. $C_{11}H_{14}Cl_2N_2O$ requires C, 50.59; H, 5.40; N, 10.73%); obtained as a 3.3:1 ratio of rotamers.

N-*Benzyl*-N-*phenyldichloroacetohydrazide* **3d**, an off-white solid, m.p. 132–134 °C (18 mg, 43%); ν_{max}/cm^{-1} 3233 (NH), 1691 (CO), 1600, 1498; δ_H(90 MHz) 4.6 (2 H, s, NCH_2 in rotamer B), 4.75 (2 H, s, NCH_2 in rotamer A), 5.9 (1 H, s, $CHCl_2$ in rotamer A), 6.35 (1 H, s, $CHCl_2$ in rotamer B), 6.8–7.1 (3 H, m, NPh *m*- and *p*-H), 7.2–7.4 (2 H, m, NPh *o*-H) and 8.0 (1 H, br s, NH) (ratio of isomers is 5:1); *m*/*z* 310 and 308 (3 and 5%, respectively, M^+), 219 and 217 (2.2 and 3.3%, $M^+ - CH_2Ph$), 91 (100%, CH_2Ph). *N*-Benzylaniline (5 mg, 20%) was also obtained from this reaction as a yellow oil; δ_H(90 MHz) 4.2 (2 H, s, NCH_2) and 6.8–7.6 (10 H, m, NPh and Ph); *m*/*z* 182 (56%, M^+), 105 (100%, $M^+ - Ph$) and 77 (45%, Ph). An authentic sample of the hydrazide was prepared by the reaction of dichloroacetyl chloride and the parent hydrazine (Found: C, 58.0; H, 4.5; N, 8.9. $C_{15}H_{14}Cl_2N_2O$ requires C, 58.27; H, 4.56; N, 9.06%); δ_C(22.5 MHz) 58 (CH_2N), 67 ($CHCl_2$), 115, 122, 129, 130, 131, 137, 149 and 164 (CO); obtained as a 5:1 ratio of rotamers.

N-*Allyl*-N-*phenyldichloroacetohydrazide* **3e**, a dark-brown oil (20 mg, 49%) (Found: M^+, 258.0327. $C_{11}H_{12}Cl_2N_2O$ requires *M*, 258.0327); ν_{max}/cm^{-1} 3222 (NH), 1692 (CO), 1601 and 1496; δ_H(270 MHz) 4.1 (2 H, dt, $J < 1$, J' 6.75, CH_2C=), 5.35 (2 H, m, =CH_2), 5.75–6.0 (1 H, m, CH=), 6.0 (1 H, s, $CHCl_2$ in rotamer A), 6.5 (1 H, s, $CHCl_2$ in rotamer B), 6.9–7.1 (3 H, m, NPh *m*- and *p*-H), 7.25–7.35 (2 H, m, NPh *o*-H), 8.1 (1 H, br s, NH) (ratio of rotamers is *ca.* 3:1); δ_C(68 MHz) 56 (CH_2N), 66 ($CHCl_2$), 114, 116, 121, 123, 130, 132, 148 and 163 (CO); *m*/*z* 260 and 258 (5.5 and 8.6%, respectively, M^+), 219 and 217 (3.7 and 5.7%, $M^+ - C_3H_5$), 149 (33%), 131 (36%), 107 (43%) and 77 (100%, Ph).

N-*Phenyl*-N-*prop*-2-*ynyldichloroacetohydrazide* **3f**, an orange solid (12 mg, 30%), m.p. 116–118 °C; ν_{max}/cm^{-1} 3297 (NH), 1705 (CO), 1601 and 1498; δ_H(270 MHz) 2.25 (1 H, t, *J* 2, CH), 4.25 (2 H, d, *J* 2, CH_2N), 6.0 (1 H, s, $CHCl_2$ in rotamer A), 6.45 (1 H, s, $CHCl_2$ in rotamer B), 6.85–7.1 (3 H, m, NPh *m*- and *p*-H), 7.15–7.35 (2 H, m, NPh *o*-H) and 8.15 (1 H, br s, NH) (ratio of rotamers is 2.5:1); an authentic sample was prepared by the reaction of dichloroacetyl chloride with the parent hydrazine (Found: C, 51.5; H, 4.1; N, 10.8. $C_{11}H_{10}Cl_2N_2O$ requires C, 51.38; H, 3.92; N, 10.9%); δ_C(22.5 MHz) 44 (CH_2N), 67 ($CHCl_2$), 80 (CH), 116, 122, 130 and 164 (CO); *m*/*z* 258 and 256 (16.5 and 26% respectively, M^+), 219 and 217 (18 and 27.5%, $M^+ - C_3H_3$), 184 (48%), 145 (36%), 129 (49%), 107 (49%) and 77 (100%, Ph).

N,N-*Diphenyldichloroacetohydrazide* **3g**, a yellow solid, m.p. 175–177 °C (14 mg, 34%); δ_H(90 MHz) 6.0 (1 H, s, $CHCl_2$ in rotamer A), 6.6 (1 H, s, $CHCl_2$ in rotamer B), 6.9–7.4 (10 H, m, NPh), 8.5 (1 H, br s, NH) (ratio of rotamers is *ca.* 8:1). Diphenylamine (7 mg, 28%) [ν_{max}/cm^{-1} 3400 (NH), 1593 and 1494; *m*/*z* 169 (100%, M^+)] and *N*,*N*-diphenylhydrazine (9.5 mg, 30%) [trapped as its acetone hydrazone: ν_{max}/cm^{-1} 1589 and 1489; *m*/*z* 224 (51%, M^+) and 168 (100%, NPh_2)] were also formed in this reaction. An authentic sample of the hydrazide was prepared by reaction of dichloroacetyl chloride with the parent hydrazine (Found: C, 56.7; H, 4.0; N, 9.3. $C_{14}H_{12}Cl_2N_2O$ requires C, 56.97; H, 4.10; N, 9.49%); ν_{max}/cm^{-1} 3256 (NH), 1696 (CO), 1591 and 1496; *m*/*z* 296 and 294 (16 and 25%, respectively, M^+), 183 (100%, $M^+ - COCHCl_2$) and 77 (34%, Ph); δ_C (22.5 MHz) 67 ($CHCl_2$), 121, 125 and 130.

Reaction of Dichlorobis(N,N-*dimethyldithiocarbamato*)[*hydrazido*(2−)]*molybdenum*(VI) *Complexes with Silver Nitrate.*—Complex **5a** (0.1 g, 0.19 mmol) was stirred in degassed alcohol (7 cm^3) with silver nitrate (0.109 g, 0.64 mmol) in the dark at room temperature under argon for 15 h. The mixture was opened to air for 2 h and then the light-grey solid (113 mg) was filtered off and the filtrate was concentrated to a brown oil. The concentrate was chromatographed on silica gel using ether–LP (1:1) as eluent.

In methanol was obtained 4-methoxy-2-nitro-*N*-methylaniline **14a** (10 mg, 30%) as a red solid, m.p. 96–98 °C (lit.,[20] 98–100 °C); ν_{max}/cm^{-1} 3384 (NH), 1574, 1522 (NO_2), and 1350 (NO_2); δ_H(270 MHz) 3.0 (3 H, d, *J* 5.5, NMe), 3.8 (3 H, s, OMe), 6.85 (1 H, d, *J* 9, 6-H), 7.2 (1 H, dd, *J* 3, *J'* 9, 5-H), 7.6 (1 H, d, *J* 3, 3-H) and 8.0 (1 H, br s, NH); *m*/*z* 182 (100%, M^+), 167 (22%, $M^+ - Me$), 165 (8%, $M^+ - OH$), 136 (34%, $M^+ - NO_2$) and 121 (42%); followed by 4-*methoxy*-2-*nitro*-N-*methyl*-N-*nitrosoaniline* **15a** as an orange gum (5.5 mg, 14%); ν_{max}/cm^{-1} 1572, 1542 (NO_2), 1456 and 1348 (NO_2); δ_H(270 MHz) 3.4 (3 H, s, NMe), 3.95 (3 H, s, OMe), 7.3 (1 H, dd, *J* 3, *J'* 9, 5-H), 7.4 (1 H, d, *J* 9, 6-H) and 7.6 (1 H, d, *J* 3, 3-H); *m*/*z* 211 (0.5%, M^+), 181 (57%, $M^+ - NO$), 148 (100%) and 133 (69%); an authentic sample was made by *N*-nitrosation[23] of **14a** (Found: C, 45.8; H, 4.3; N, 19.7. $C_8H_9N_3O_4$ requires C, 45.50; N, 4.30; N, 19.90%).

In ethanol was obtained 4-*ethoxy*-2-*nitro*-N-*methyl*-N-*nitroaniline* **15b** (11.5 mg, 27%) as an orange oil; δ_H(270 MHz) 1.45 (3 H, t, Me), 3.4 (3 H, s, NMe), 4.15 (2 H, q, CH_2O), 7.2 (1 H, dd, *J* 3, *J'* 9, 5-H), 7.4 (1 H, d, *J* 9, 6-H), 7.6 (1 H, d, *J* 3, 3-H); *m*/*z* 225 (0.1%, M^+), 195 (31%, $M^+ - NO$), 162 (61%) and 134 (100%); containing traces of 4-*ethoxy*-2-*nitro*-N-*methylaniline* by ^1H NMR spectroscopy (doublet at 6.8, *J* 9).

In isopropyl alcohol was obtained 4-*isopropoxy*-2-*nitro*-N-*methyl*-N-*nitrosoaniline* (2 mg, 4.5%) as a yellow oil; δ_H(270 MHz) 1.4 (6 H, d, $CHMe_2$), 3.4 (3 H, s, NMe), 4.65 (1 H, sept. $CHMe_2$), 7.25 (1 H, dd, *J* 3, *J'* 9, 5-H), 7.4 (1 H, d, *J* 9, 6-H) and 7.6 (1 H, d, *J* 3, 3-H); *m*/*z* 239 (0.2%, M^+), 209 (10%, $M^+ - NO$), 176 (17%), 167 (18%), 151 (31%) and 134 (100%); containing traces of 4-*isopropoxy*-2-*nitro*-N-*methylaniline* as indicated by ^1H NMR spectroscopy (doublet at 6.9, *J* 9).

In methanol in the presence of freshly distilled styrene (67 mg, 0.64 mmol) was obtained α-nitroacetophenone oxime[28] as an orange oil (16 mg, 82% with respect to **5a**); ν_{max}/cm^{-1} 3310 (br,

OH), 1565 (C=N), 1557 (NO_2) and 1373 (NO_2); δ_H(270 MHz) 5.7 (2 H, s, CH_2NO_2), 7.4–7.5 (3 H, m, Ph, *m*- and *p*-H), 7.6–7.7 (2 H, m, Ph, *o*-H) and 9.2 (1 H, br s, OH); δ_C(125 MHz) 68 (CH_2 by DEPT 135), 126 (CH by DEPT 90), 129 (CH by DEPT 90), 130 (CH by DEPT 90), 133 (C by DEPT 135), 148.5 (C by DEPT 135); *m/z* 180 (4%, M^+), 146 (11% – NH_2OH – H), 134 (5%, $M^+ - NO_2$), 121 (24%, $M^+ - CH_2NO_2 + H$) and 103 (100%, M^+ – Ph).

5-Methoxy-2-nitro-N-methylaniline.—5-Methoxy-2-nitroacetanilide[22] was *N*-methylated and deacetylated according to the method of Wilshire[20] to give an ochre-coloured solid, m.p. 93–96 °C (Found: C, 53.0; H, 5.4; N, 15.3. $C_8H_{10}N_2O_3$ requires C, 52.7; H, 5.49; N, 15.38); δ_H(270 MHz) 3.0 (3 H, d, NMe), 3.9 (3 H, s, OMe), 5.1 (1 H, br s, NH), 6.45 (1 H, d, *J* 9.5, 4-H), 7.6 (1 H, d, *J* 3, 6-H) and 7.9 (1 H, dd, *J* 3, *J'* 9.5, 3-H); *m/z* 182 (100%, M^+), 167 (45%, M^+ – Me), 136 (12%, $M^+ - NO_2$), 121 (17%) and 93 (17%).

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