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Bulk Gold-Catalyzed Oxidations of Amines and Benzyl Alcohol Using Amine N-Oxides as Oxidants

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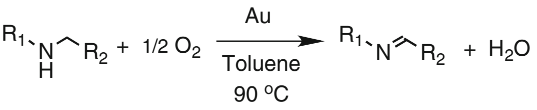
Abstract *Bulk* gold powder (~50 µm) catalyzes the oxidative dehydrogenation of amines to give imines using amine N-oxides (R_3N-O) as the oxidant. The reaction of dibenzylamine ($PhCH_2$–NH–CH_2Ph) with N-methylmorpholine N-oxide (NMMO) in the presence of gold powder at 60 °C produced N-benzylidenebenzylamine (PhCH=N–CH_2Ph) in 96% yield within 24 h. Benzyl alcohol was oxidized by NMMO to benzaldehyde in >60% yield in the presence of gold powder. Although O_2 was previously shown to oxidize amines in the presence of bulk gold, it is surprising that gold is also capable of catalyzing the oxidation of amines using amine oxides, which are chemically so different from O_2.

Keywords Gold · Oxidative-dehydrogenation · Catalysis · Amine N-oxide · Imine · Amine · Oxidation · Alcohol

1 Introduction

Nanogold particles (<5 nm) supported on various oxide supports are known to catalyze numerous reactions [1–7], including the oxidation (O_2) of CO, hydrocarbons, and alcohols, while *bulk* gold powder has traditionally been thought to be a poor catalyst [1]. However, our group has recently found that bulk gold also catalyzes several oxidations in which O_2 is the oxidant. These include the reaction of isocyanides with amines to produce carbodiimides [8] or ureas [9], reactions of carbon monoxide with primary amines to afford ureas [10], and reactions of diazoalkanes with amines to give enamines [11]. In addition, bulk gold catalyzes the oxidative dehydrogenation of amines to imines using O_2 as the oxidant (Eqs.1–3) [12, 13]. This reaction has drawn much recent interest, as nanogold supported on ceria [14, 15], polystyrene [14], alumina [16], titania [16], and carbon [16, 17] has also been found to catalyze the oxidative dehydrogenation of amines using O_2.



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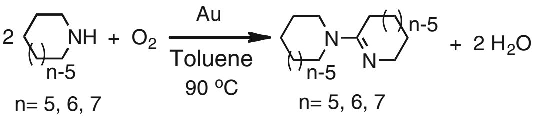

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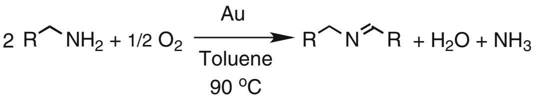

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In expanding the scope of gold catalysis, we examined amine N-oxides (R_3N–O) as the oxidizing agent in the oxidative dehydrogenation of amines. The only other previously reported oxidant in the bulk Au-catalyzed oxidative dehydrogenation of amines is NO_2, which exhibited comparable activity to O_2 in reactions of pyrrolidine and 1,2,3,4-tetrahydroisoquinoline to give their imines [18]. Prior to our studies of amine oxides, R_3N–O compounds had been used as oxygen atom donors and oxidizing agents in a variety of homogeneous reactions [19]. However, their oxidizing reactivities are typically very different than those

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of O_2, which is not surprising because of the very different properties of the R_3N–O and O_2 molecules. Therefore, the goal of the present investigation was to assess the effectiveness of bulk gold as a catalyst for the oxidative dehydrogenation of amines using amine oxides. As reported herein, amine oxides do indeed oxidize amines to give the same products as O_2 in the presence of a bulk gold catalyst.

2 Experimental Section

Dibenzylamine, piperidine, pyrrolidine, 1,2,3,4-tetrahydroisoquinoline (THIQ), and benzyl alcohol were purchased commercially and purified by heating at reflux with CaH_2 for 12 h and distilling under argon before use. N-benzylidenebenzylamine and benzaldehyde were purchased from Sigma-Aldrich and used as received. Amidine-5 [20], amidine-6 [20], and 3,4-dihydroisoquinoline [12] were synthesized as described previously. Acetonitrile-d3 was heated at 80 °C with CaH_2 for 8 h, and then purified by a trap-to-trap distillation under reduced pressure. N-methylmorpholine N-oxide (NMMO), trimethylamine N-oxide (Me_3NO), and pyridine N-oxide (PyNO) were sublimed under reduced pressure. Gold powder was prepared from $HAuCl_4$ as described previously [21]. The powder, which was previously characterized by electron microscopy [13, 21], consisted of large particles (5–50 μm). The reactions were run in NMR tubes (17×0.3 cm ID, ~ 1.7 mL volume), which were loaded with 0.20 g Au and then sealed with a high-vacuum Teflon stopcock. The tubes were then evacuated and back filled three times with argon, sealed under reduced pressure, and then brought into a nitrogen-atmosphere glove box. After loading the tubes with the desired concentrations of reactants (vide infra), they were removed from the glovebox and heated in an oil bath at 60 °C. The reactions were monitored by ^1H NMR on a Varian MR-400 or a Bruker DRX-400 spectrometer with Ph_3CH as the internal standard. ^1H NMR peak positions were referenced against the residual proton signal of CD_3CN ($\delta = 1.94$ ppm). Previous work showed that the gold powder loses some catalytic activity when it is reused in successive reactions [20, 21]. In this study we used the most active form of Au in all reactions. This catalyst was prepared from the initial dull brown Au that was produced by reduction of $HAuCl_4$ [21]. The dull Au was converted to an active and lustrous golden form by an oxidative dehydrogenation reaction of Bn_2NH and NMMO in CH_3CN for 24 h at 60 °C. After being used in this reaction, the batch of Au powder was collected and cleaned as described previously [21]. This Au powder was used in all of the studies reported herein.

2.1 General Procedure for Oxidative Dehydrogenation of Amines Using Amine N-Oxides

In a glove box, an CD_3CN-stock solution was prepared with the desired amine and internal standard (30 mM amine, 18.8 mM Ph_3CH). A second CD_3CN-stock solution of the amine N-oxide (330 mM) was also prepared. The amine/Ph_3CH solution (0.40 mL) and amine N-oxide solution (0.20 mL) were added to an NMR tube containing 0.20 g Au to give a 0.60-mL mixture with the desired amine and amine N-oxide concentrations, 20 and 110 mM, respectively. The tube was sealed with a high-vacuum Teflon stopcock, brought out of the glovebox, and a ^1H NMR spectrum was immediately recorded. The tube was then heated in an oil bath at 60 °C and periodically analyzed by NMR; concentrations of reactants and products are reproducible within approximately ± 3%. Products were identified by comparing their ^1H NMR spectra with those of authentic compounds.

2.2 General Procedure for Decomposition of Amine N-Oxides

In a glove box, CD_3CN-stock solutions of the amine N-oxide (0.20 mL, 330 mM) and Ph_3CH (0.20 mL, 75 mM) were added to an NMR tube containing 0.20 g Au. Then 0.20 mL CD_3CN was added to give a 0.60-mL mixture with the desired amine N-oxide concentration of 110 mM. The tube was then sealed with a high-vacuum Teflon stopcock, removed from the glovebox, and a ^1H NMR spectrum was immediately recorded. The tube was then heated in an oil bath at 60 °C and periodically analyzed by NMR.

2.3 Characterization of 4-Methylmorpholine-2,3-dione

Two NMR-tube reactions of the Au-catalyzed decomposition reaction of NMMO (0.20 g Au, 220 mM NMMO, 0.60 mL CD_3CN) were heated at 60 °C. After 48 h, the solutions were transferred from the Au by pipet into a single flask, the volatile components were removed under reduced pressure, and the product was characterized spectroscopically. IR (film on NaCl, ν [cm^{-1}]): 1757 (s, C=O), 1689 (s, C=O), 1354 (m), 1186 (m), 1063 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.53$ (t, $^3J_{H,H} = 5.2$ Hz, 2 H, CH_2), 3.69 (t, $^3J_{H,H} = 5.2$ Hz, 2 H, CH_2), 3.16 (s, 3 H, CH_3). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 156.3$ (CO), 153.7 (CO), 65.1 (CH_2), 47.0 (CH_2), 34.9 (CH_3). MS (EI): 128 $[M]^+$. These data match reported values for this compound [22].

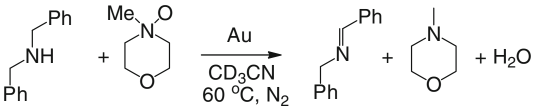
2.4 General Procedure for Oxidative Dehydrogenation of Benzyl Alcohol Using NMMO

CD_3CN-stock solutions of benzyl alcohol (BnOH) and Ph_3CH (0.40 mL solution: 30 mM BnOH, 18.8 mM Ph_3CH) and NMMO (0.20 mL, 90–540 mM) were added to an NMR tube containing 0.20 g Au to give a 0.60-mL mixture with the desired alcohol and amine N-oxide concentrations. The tube was sealed with a high-vacuum Teflon stopcock, taken out of the glovebox, and a ^1H NMR spectrum was immediately recorded. The tube was then heated in an oil bath at 60 °C and periodically analyzed by NMR.

3 Results and Discussion

3.1 Au-Catalyzed Oxidative Dehydrogenation of Dibenzylamine Using Various Amine N-Oxides or O_2

In previous work, we found that bulk Au powder was an effective catalyst for the oxidative dehydrogenation of secondary amines using molecular oxygen as the oxidant (Eqs. 1–3) [12]. In the current studies, we initially examined the oxidative dehydrogenation of Bn_2NH, using three different amine N-oxides, NMMO, Me_3NO, and PyNO (Fig. 1) in CD_3CN at 60 °C (Fig. 1). Within 24 h, a 96% yield of N-benzylidenebenzylamine (100% conversion) was afforded using NMMO as the oxidant (Eq. 4). A lower yield (77%) of imine product was obtained over the same time period when Me_3NO was used as the oxidant, with a Bn_2NH conversion of only 80%.



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The less basic pyridine N-oxide, PyNO, generated only a 6% yield of the imine product under the same conditions (Fig. 1), while the dibenzylamine remained largely unreacted (6% conversion). The reactivities of the amine N-oxides therefore decrease as their basicities decrease as reflected by the pK_as of their conjugate acids: $NMMOH^+$ (4.75) [23] $>Me_3NOH^+$ (4.56) [24] $>PyNOH^+$ (0.79) [25]. To verify that the amine N-oxide and Au were necessary for the transformation, two separate control reactions were run. In one case, the reaction was run without NMMO. After 48 h at 60 °C, less than a 2% yield of the imine was produced. No Au was loaded into the second control reaction, and no conversion of the amine to the imine was observed after heating for 48 h at 60 °C. To test for catalytically active colloidal or soluble gold complexes, a reaction was set up in the glovebox, with the same concentrations of NMMO and Bn_2NH as above, but with a solution volume of 0.80 mL and the tube was sealed with a rubber septum. After 4 h, half (0.40 mL) of the solution at 60 °C was transferred by syringe to another NMR tube. ^1H NMR analysis of both tubes showed a 22% yield of the imine product. After heating at 60 °C for 24 h, an NMR analysis of the tube that contained the gold powder gave a 92% yield of the imine product, while that containing only the reactant solution (with no powdered Au) still showed only 22% of the product. These results clearly show that the bulk Au powder was the active catalyst in this reaction.

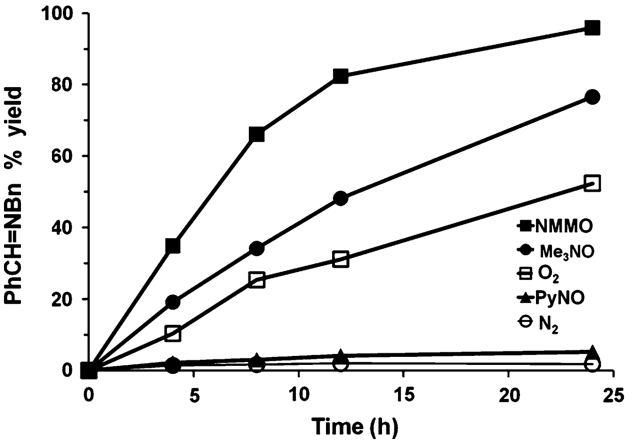


Fig. 1 Performance of different oxidants in the catalytic oxidative dehydrogenation of Bn_2NH to PhCH=NBn. Conditions: Bn_2NH (20 mM), oxidant: amine N-oxide (110 mM), O_2 (~1 L, ~1 atm) or N_2 (1 atm), Au (0.20 g), CD_3CN (0.60 mL), 60 °C

To compare the reactivity of O_2 to those of the amine N-oxides, the oxidative dehydrogenation of Bn_2NH was setup in the same manner as above, using O_2 in place of the amine N-oxide. After the NMR tube containing 20 mM Bn_2NH and 0.20 g Au in 0.60 mL CD_3CN was sealed with a rubber septum, it was removed from the glovebox. After obtaining an initial ^1H NMR spectrum, a syringe needle, attached to a balloon of O_2 (~ 1 L, ~ 1 atm), was inserted into the rubber septum of the NMR tube. At 60 °C, the O_2 reaction was found to be much slower than those of both NMMO and Me_3NO, producing only a 52% yield of imine (57% conversion) after 24 h (Fig. 1). Extending the reaction time to 48 h increased the yield to 85% (89% conversion).

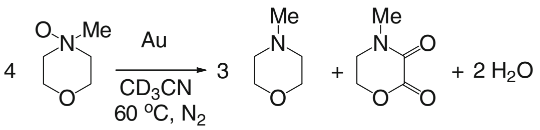
In an attempt to determine a rate law for the Au-catalyzed oxidative dehydrogenation of Bn_2NH with NMMO, initial rates of the reaction were measured by NMR at different amine concentrations and a constant initial NMMO concentration. The NMR tube reactions were heated at 50 °C while spinning at 20 Hz in an NMR instrument. Increasing the amine concentration (5–100 mM) had a negligible effect on the rate of the reaction, indicating that the reaction was zero order in amine concentration. The complementary rate studies with increasing NMMO concentrations (16–50 mM), while starting with the same Bn_2NH concentration, always increased the rate. However, it was difficult to generate sufficiently reproducible rates (possibly caused by adsorption of by-products during the course of the reaction) to define a reaction order with respect to NMMO. Thus, it is only possible to state qualitatively that the rate of reaction increases at higher NMMO concentrations. These limited studies suggest that the gold surface is saturated with the amine at all concentrations, which accounts for the zero-order dependence on amine concentration. The increasing rate with an increase in R_3N–O concentration is consistent with a step in the mechanism in which R_3N–O competes with amine for adsorption sites on the gold surface. The faster rates with increasing basicity of the R_3N–O (Fig. 1) also support a step involving competitive adsorption of the R_3N–O. Further mechanistic interpretation is not possible and would be highly speculative.

In reactions that used an amine N-oxide as the oxidant, ^1H NMR analysis revealed that the reduction product was the corresponding tertiary amine (e.g., NMM, Me_3N, or pyridine). In the oxidative dehydrogenation reaction of Bn_2NH with NMMO, the yield of tertiary amine (NMM) closely corresponded with the yield of the imine product up to ca. 80% conversion of the Bn_2NH, after which the NMM began to form at a faster rate than the imine. This indicated that NMMO was being consumed by another process that did not involve the oxidation of Bn_2NH (vide infra).

3.2 Au-Catalyzed Decomposition of Amine N-Oxides

It was previously reported that NMMO decomposed above 120 °C in inert dihalobenzene solvents, to give NMM and morpholine as major products, and formaldehyde as a minor product [26, 27]. In our studies, no decomposition of NMMO (110 mM in 0.6 mL CD_3CN) occurred at 60 °C, in the absence of Au. We then investigated the gold-catalyzed decomposition of amine N-oxides, under the conditions used for the oxidative dehydrogenation of Bn_2NH. In an NMR-tube reaction, 110 mM NMMO in 0.60 mL CD_3CN and 0.20 g Au powder were heated at 60 °C. After 48 h, NMMO was no longer observable by ^1H NMR, and 74% of the starting material was converted to NMM.

In addition to NMM, a new product was identified with ^1H NMR peaks at 4.49 (t, $^3J_{H,H} = 5.2$, 2H, CH_2), 3.69, (t, $^3J_{H,H} = 5.2$, 2H, CH_2), and 3.03 (s, 3H, CH_3) ppm in CD_3CN. The isolated compound exhibited IR peaks for ester and amide carbonyl groups at 1,757 and 1,689 cm^{-1}, respectively, and the mass spectrum exhibited a molecular ion peak at 128 m/z. The IR, ^1H NMR, and mass values are in agreement with published data for 4-methyl-morpholine-2,3-dione (Eq. 5) [22]. Approximately 14% of the NMMO was converted to this dione, as determined by ^1H NMR. Since this product contains two carbonyl groups, 28% of the oxygen content of the initial NMMO is incorporated into the dione product. The four hydrogen atoms that are lost during the conversion of NMMO to the dione are most likely consumed by another two oxygen atoms to produce two equivalents of water, which would account for an additional 28% of the oxygen content from the NMMO. Although the fate of a majority of the oxygen (56%) in the initial NMMO was determined, the mass balance was less than quantitative, indicating that unidentified oxygen-containing products must also be formed. Unfortunately, quantification of water by ^1H NMR was not possible due to overlapping peaks with NMM. GC–MS analysis of the reaction mixture also showed the presence of a trace product with a mass of 115 m/z. Compounds of this mass could be either N-methylmorpholinone or 4-formylmorpholine.



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The decomposition of Me_3NO was also investigated under the same conditions as those for NMMO (0.20 g Au, 110 mM Me_3NO, 0.6 mL CD_3CN, 60 °C). In addition to the expected Me_3N, dimethylformamide (DMF) (confirmed by adding authentic DMF to the reaction mixture in the NMR tube and comparing the peak shifts of the formyl and methyl protons) was also formed (Eq. 6, Fig. 2).

$$2\,Me_3NO \xrightarrow[\substack{CD_3CN\\ 60\ ^\circ C,\ N_2}]{Au} Me_3N + HCONMe_2 + H_2O \tag{6}$$

After 72 h, all of the Me_3NO was consumed, resulting in the formation of DMF (39%) and Me_3N (26%). The nonstoichiometric Me_3N/DMF ratio is likely due to the volatility of Me_3N (BP = 3 °C). The production of DMF involves the consumption of an equivalent amount of oxygen atoms (Eq. 6), which would utilize 78% of the oxygen in the original Me_3NO. Therefore, other unidentified oxygen-containing products must also form. ^1H NMR integration of a semi-broad water peak at 2.19 ppm

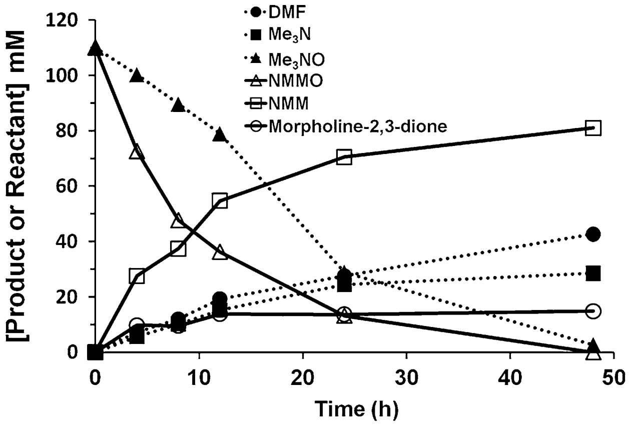


Fig. 2 Au-catalyzed decomposition reactions of amine N-oxides. Conditions: Amine N-oxide (110 mM), Au (0.20 g), CD_3CN (0.60 mL), 60 °C

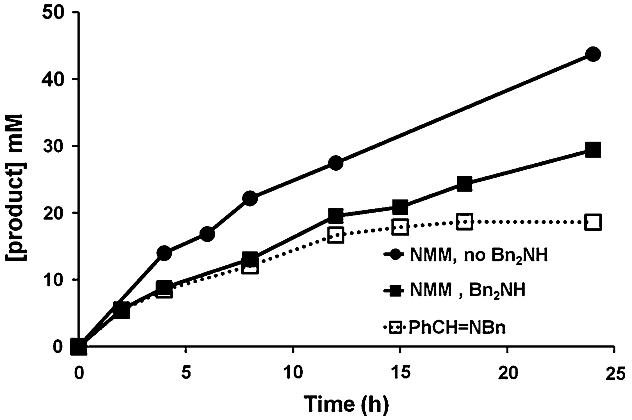
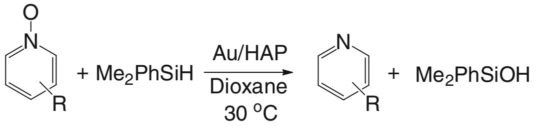


Fig. 3 Effect of the presence of Bn_2NH on the decomposition of NMMO. Conditions: NMMO (110 mM), Bn_2NH (20 mM, if applicable), Au (0.20 g), CD_3CN (0.60 mL), 60 °C

(partially overlapped with the Me_3N peak), accounted for less than 46% of the oxygen content, with a large uncertainty in the integration due to the overlapping signals.

Qualitative rates of the decomposition of NMMO and formation of the NMM product were compared in the presence and absence of Bn_2NH. As shown in Fig. 3, NMM and PhCH=NBn form in about a 1:1 ratio up to 8 h (80% conversion). At this time (8 h), the production of 4-methylmorpholine-2,3-dione was first observed and the production of NMM began to occur at a faster rate than the formation of the imine. The formation of the dione is consistent with the increased rate of decomposition of NMMO (Eq. 5) under conditions of low Bn_2NH concentration.

The only previous studies of Au-catalyzed deoxygenation reactions of amine N-oxides were those using gold nanoparticles supported on hydroxyapatite (HAP) or titania (TiO_2) in reactions with either dimethylphenylsilane (Eq. 7) [28] or CO/H_2O (Eq. 8) [29].



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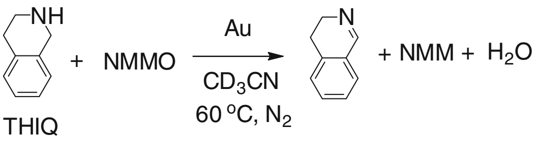
R = H, *p*-Me, *p*-Ph, *p*-CN, *p*-CH_2OH, *m*-$C(O)OCH_3$

$$\begin{gathered}R_3NO + CO \xrightarrow[\text{Acetone}]{Au/TiO_2} R_3N + CO_2 \\ H_2O,\ 30\,^\circ C \\ R_3NO = PyNO,\ Et_3NO\end{gathered} \tag{8}$$

3.3 Au-Catalyzed Oxidative Dehydrogenation of Other Amines Using NMMO

The oxidative dehydrogenations of THIQ, pyrrolidine [$(CH_2)_4NH$], and piperidine [$(CH_2)_5NH$] were investigated using the same conditions that were used for Bn_2NH. The overall product yields for each of these amines were lower than that for Bn_2NH (Fig. 4). The same imine products (Eqs. 9, 10) [12] were obtained as when molecular oxygen was used as the oxidant (Eqs. 1, 2). When the reaction time was extended from 24 to 48 h in the oxidative dehydrogenation of THIQ (Eq. 9), the yield of imine increased from 61% (85% conversion) to 70% (100% conversion), while the yield of the amidine-5 product from the pyrrolidine reaction (Eq. 10) increased from 65 to 91% over the same time period.



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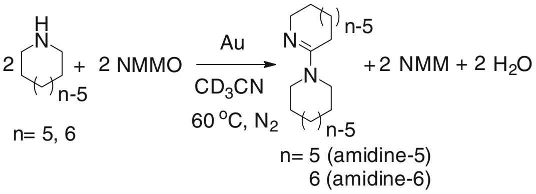


(10)

The reaction of the primary amine benzylamine ($BnNH_2$) and NMMO was studied under the same conditions as those used for the secondary amines. N-benzylidenebenzylamine was the only product that resulted from the oxidative dehydrogenation of the amine (Eq. 11), as was also observed when molecular oxygen was used as the oxidant (Eq. 3) [13]. The yield of PhCH=NBn after 24 h, was 33% (34% conversion), while the yield increased further to 45% (46% conversion) after 48 h. The reaction

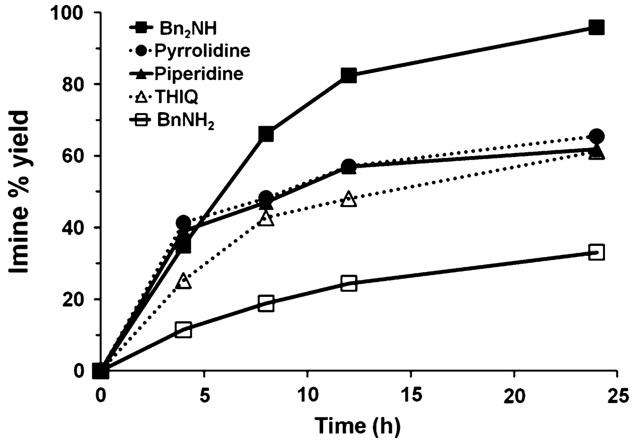
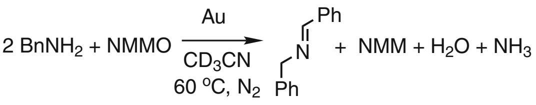


Fig. 4 Percent yield of imine products (Eqs. 4, 9–11) from various amines using NMMO as the oxidant. Conditions: amine (20.0 mM), NMMO (110 mM), Au (0.20 g), CD_3CN (0.60 mL), 60 °C

most likely involves an initial oxidation of the amine to an imine intermediate which is attacked by an additional molecule of $BnNH_2$ to give the final PhCH=NBn product, as previously proposed for the bulk gold catalyzed reaction using O_2 as the oxidant [13].



$$2\,BnNH_2 + NMMO \xrightarrow[60\,^{\circ}C,\,N_2]{Au,\ CD_3CN} PhCH{=}NCH_2Ph + NMM + H_2O + NH_3 \quad (11)$$

3.4 Au-Catalyzed Oxidative Dehydrogenation of Benzyl Alcohol Using NMMO and O_2

The oxidation of BnOH (20 mM) with NMMO (110 mM) in CD_3CN was also investigated using Au powder as the catalyst (Eq. 12) at 60 °C. This afforded benzaldehyde (PhCHO) in 42% yield (65% conversion) after 24 h. When the reaction time was extended from 24 to 48 h, the yield of PhCHO increased to only 52% (77% conversion). In an attempt to optimize the aldehyde yield, the NMMO concentration was first decreased from 110 to 30 mM, which led to a decrease in the aldehyde yield (47, 50% conversion) after 48 h (Fig. 5). Increasing the NMMO concentration to 180 mM improved the PhCHO yield to 57%, (69% conversion) after 48 h. An increase in temperature also had a positive effect on the reaction. At 85 °C (110 mM NMMO), the reaction rate was fastest and the highest yield of PhCHO (63, 76% conversion) was afforded after 48 h.

$$BnOH + NMMO \xrightarrow[\substack{CD_3CN \\ 60\,^{\circ}C,\ N_2}]{Au} PhCHO + NMM + H_2O \quad (12)$$

To verify that the gold catalyst was necessary for this oxidation, a control reaction was performed under identical conditions (20 mM BnOH, 110 mM NMMO, 0.6 mL CD_3CN, 60 °C), but without gold powder. No conversion of benzyl alcohol was observed. As compared to NMMO, O_2 was a far inferior oxidant in this reaction, as the oxidative dehydrogenation of benzyl alcohol using O_2 (~1 L, ~1 atm) at 60 °C, resulted in a substantially slower rate with only a 7% yield of PhCHO, while 91% BnOH remained unreacted after 48 h (Fig. 5). Although many nanogold catalysts [7] supported on hydrotalcite [30], titania [31], ceria [31], and gallia [32] catalyze this reaction with O_2, only recently was bulk gold reported to catalyze this reaction and then only under more strenuous conditions (90 °C, 5 atm O_2) [33].

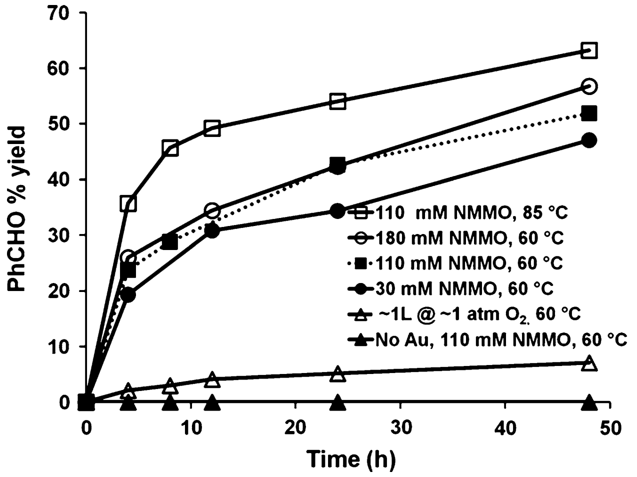


Fig. 5 Percent yield of benzaldehyde in the Au-catalyzed reaction of benzyl alcohol with NMMO and O_2. Conditions (unless otherwise noted): BnOH (20 mM), NMMO (30–180 mM), Au (0.20 g), CD_3CN (0.60 mL)

4 Conclusions

The results described in this manuscript show that aliphatic amine N-oxides are effective oxidants in bulk Au-catalyzed oxidative dehydrogenation reactions of both amines and benzyl alcohol. Although details of the mechanisms have not been established for the reactions of either $R_3N{-}O$ or O_2, they are undoubtedly different because of the very dissimilar natures of these oxidants. However, it important to note that bulk gold is capable of catalyzing reactions using both oxidants. The basicity of the amine N-oxide strongly influences the oxidative dehydrogenation of Bn_2NH to $PhCH{=}N{-}CH_2Ph$, as the reactions were much faster with the most basic amine N-oxides (NMMO and Me_3NO) than with the less basic PyNO. The optimum yield for this reaction is 96% with a TON of 10 based on an estimate of the number of surface gold atoms [34] and assuming that all were active sites. The discoveries reported in this manuscript further expand the range of reactions that are catalyzed by bulk gold.

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