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Bulk Gold-Catalyzed Reactions of Diazoalkanes with Amines and O_2 to Give Enamines

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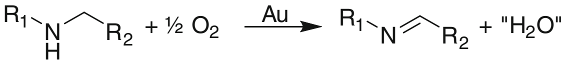
Abstract Bulk gold powder, consisting of approximately 5–50 μm particles, catalyzes reactions of diazoalkanes *E*(H)C=N_2, where *E* is CO_2Et or PhC(O), with amines R^1R^2NH and O_2 to give enamine products (R^1R^2N)(*E*)C=CH(*E*) in 58–94% yield. The reactions are proposed to occur by initial formation of surface-bound (*E*)(H)C: carbene groups that are attacked by nucleophilic amines. The enamine products are very different than those obtained in reactions catalyzed by homogeneous transition metal complexes. These reactions of diazoalkanes, amines, and O_2 represent a new type of bulk gold-catalyzed reaction.

Keywords Gold · Catalysis · Amines · Enamines · Oxidation

1 Introduction

Nano-sized gold particles (<5 nm) supported on metal oxides catalyze a variety of reactions including CO, hydrocarbon and alcohol oxidation [1–8]. On the other hand, *bulk* gold metal is well-known for its poor catalytic properties [1]. However, we have shown in previous studies that bulk gold powder with particle sizes of ~1,000 nm is capable of catalyzing reactions of isocyanides (C≡N–R) with amines and O_2 to produce carbodiimides (in the case of primary amines) [9] or ureas (in the case of secondary amines) [10], and reactions of carbon monoxide CO with primary amines and O_2 to give ureas [11]. Bulk gold powder also catalyzes the oxidation (O_2) of CO to CO_2 under alkaline conditions [12]. We have also shown that primary and secondary amines with O_2 give imines (Eq. 1) using gold powder [13] and Au/Al_2O_3 (with ≥50 nm Au particles) [14]



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as catalysts. Recently, others have shown that these oxidative dehydrogenation reactions of amines are catalyzed by the nanogold catalysts Au/TiO_2, Au/C and Au/CeO_2 [15–17]. Many of our studies of bulk gold-catalyzed reactions were inspired by known reactivities of ligands (e.g., CO and C≡N–R) in transition metal complexes [18]. In one recent investigation, we used known reactions of diazoalkanes ($R_2C=N_2$) [19–24] with transition metal complexes that give carbene complexes ($M = CR_2$) to generate carbene groups (:CR_2) on gold powder surfaces. Chemical evidence for these carbenes was the observation that gold powder catalyzes the coupling of two carbene groups in the reaction: $2\ R_2C=N_2 \rightarrow R_2C=CR_2 + 2\ N_2$ [25]. For the specific case of ethyl diazoacetate (EDA), the reaction (Eq. 2) gives both *cis* and *trans* olefinic products. A variety of

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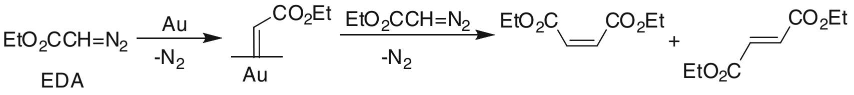

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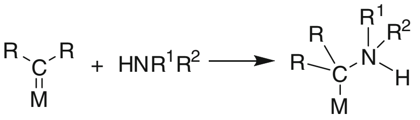
v homogeneous complexes are also known to catalyze the conversion of diazoalkanes into olefins [19–24, 26–30]. In another type of carbene reactivity, gold powder catalyzes reactions of diazoalkanes with styrenes to give cyclopropanes [25]. Carbene ligands in metal complexes are also known to be susceptible to attack by amines (Eq. 3) [31, 32]. Such a reaction is proposed to be a key step in the reaction of diazoalkanes with amines to give N–H insertion products (Eq. 4) when catalyzed by a variety of homogeneous transition metal complexes. For reviews involving catalyzed diazo compound N–H insertion reactions, see: [33–44]. For examples of highly enantioselective metal-catalyzed intermolecular carbenoid N–H insertion reactions, see: [45]. Among these catalysts is an N-heterocyclic carbene complex of Au(I) [46, 47]. Also relevant to the present report is the copper metal-catalyzed N–H insertion reaction (Eq. 5) of α-diazoacetophenone and aniline [48].



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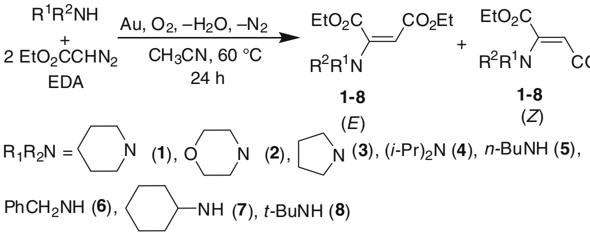
$$EtO_2CCH{=}N_2 + R^1R^2NH \xrightarrow{\text{cat.}} EtO_2CCH_2{-}NR^1R^2 + N_2 \quad (4)$$

$$PhCOCH{=}N_2 + PhNH_2 \xrightarrow{\text{Cu}} PhCOCH_2NHPh + N_2 \quad (5)$$

In the present study, we examine gold powder catalysis of the reactions of diazoalkanes with amines and O_2. If gold catalyzed any reaction of these reactants, we expected it to give N–H insertion products based on the reactions in Eqs. 4 and 5. Instead, it gives the unexpected enamine product, as illustrated by the reaction of EDA (Eq. 6). Because gold powder catalyzes other reactions of the reactants, one might also expect olefinic products from the coupling of EDA (Eq. 2) and imines from the oxidative dehydrogenation of the amines (Eq. 1). Depending on the reactants and the reaction conditions, these other products are also sometimes observed. The primary purpose of this study was to demonstrate a fundamentally new type of catalytic activity for bulk gold, which is such a poor catalyst of so many other reactions [1].



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2 Experimental Section

2.1 General Methods

Acetonitrile and 1,2-dichloroethane were refluxed under N_2 overnight with CaH_2 and distilled before use. Toluene and THF were refluxed under N_2 over sodium-benzophenone and distilled before use. $HAuCl_4$ was ordered from Strem Chemicals, Inc.; ethyl diazoacetate (EDA) and all amines were purchased from Sigma–Aldrich and used as received. α-Diazoacetophenone [49, 50], Me-MPDA [51, 52] and $PhCH{=}N_2$ [53, 54] were prepared according to literature procedures.

2.2 General Procedure for the Preparation of Gold Powder

The gold powder used in the catalytic studies was prepared as described in detail previously [25]. It involved reduction of $HAuCl_4$ with hydroquinone. The resulting gold powder was washed with methanol, treated with piranha solution (H_2O_2/H_2SO_4), washed with water, and then with methanol. Drying at 110 °C in air gave a dull brown Au powder. After one reaction of EDA with an amine and O_2, the gold powder had a shiny gold appearance and a low surface area (0.35 m^2/g) [55]. It is this shiny gold powder that was used in the catalytic reactions reported in this paper. The powder consisted of large particles (5–50 μm), which have been previously characterized by electron microscopy [14, 25]. After each use in a catalytic reaction, the gold powder was cleaned by sequential washing with CH_3CN, CH_2Cl_2, and CH_3OH. Then, it was treated with piranha solution, successively washed with water and methanol, and dried at 110 °C in air. With each use in a catalytic reaction, its catalytic activity decreased slightly. After ten uses, the gold powder was completely regenerated by dissolving it in aqua regia to form $HAuCl_4$ which was converted to Au powder by the procedures described above [25].

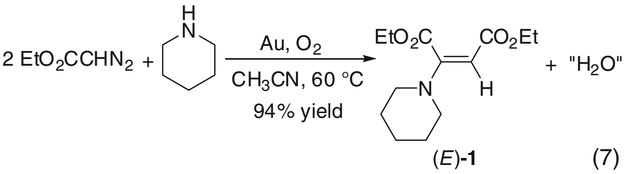
2.3 General Procedure for Gold Catalysis

A glass tube (2.5 × 18 cm, 85 mL volume) was charged with gold powder (1.0 g), and then a solution of the amine (0.6 mmol) and ethyl diazoacetate (0.2 mmol) in the desired solvent (5 mL) was added. Oxygen gas was introduced by a balloon filled with ~1 L (~40 mmol) of O_2, which was attached to a syringe needle that was inserted into the septum covering the opening of the tube. The mixture was heated to 60 °C and stirred vigorously with a magnetic stirbar for 24 h. The mixture was allowed to cool to room temperature, and the solution was decanted. Acetonitrile (3 × 5 mL) was used to wash the gold, and the solvent was removed under reduced pressure from the combined solution and washings. Triphenylmethane (0.1 mmol) was added to the crude product as an internal standard for ^{1}H NMR determination of the yield and *E*/*Z* ratios. Enamine products were identified by comparison of their ^{1}H NMR spectra with those of authentic samples. These samples were prepared [56–59] as described in the Electronic Supplementary Material where ^{1}H and ^{13}C NMR and mass spectral data for all of the products are also given.

3 Results and Discussion

3.1 Reaction of Ethyl Diazoacetate (EDA) with Piperidine and O_2

Initial studies of the reactions of diazoalkanes with amines and O_2 were performed with 0.60 mmol of piperidine and 0.20 mmol of EDA in 5 mL of CH_3CN at 60 °C using 1.00 g of shiny gold powder under 1.0 atm of O_2. The reaction generates exclusively enamine (*E*)-**1** in 94% yield after 24 h at 60 °C (Eq. 7). Products resulting from N–H insertion or dimerization of EDA were not detected. Oxygen is clearly a reactant because the reaction of EDA with piperidine occurs to only a small extent, and no other products are formed when the reaction is run under an argon atmosphere (Table 1, entry 2). The low 6% yield of (*E*)-**1** that occurs under Ar is presumably due to the presence of adventitious O_2. The gold powder is essential because no reaction occurs when EDA, piperidine, and O_2 are combined at 60 °C in acetonitrile in the absence of the gold (Table 1, entry 3). We also examined the reaction of EDA with piperidine in other solvents at 60 °C (Table 1, entries 4–8). No products resulting from N–H insertion or dimerization of EDA were observed in any of the solvents, and enamine (*E*)-**1** was formed as the major product except in $ClCH_2CH_2Cl$ where no enamine **1** or imine **1b** was detected, as piperidine reacted quantitatively with $ClCH_2CH_2Cl$ to afford N-(2-chloroethyl)piperidine and piperidine hydrochloride (entry 8). In toluene at 60 °C, an 82% yield of (*E*)-*1* was obtained (Table 1, entry 4), but at 80 °C (entry 5) a significant amount of the imine **1b** ((*E*)-**1**:**1b** = 1:1), which would be produced in the gold powder-catalyzed oxidative dehydrogenation of piperidine (Eq. 8) [13, 14], was also observed. Only 17% of (*E*)-**1** was obtained in THF solvent, the byproduct **1b** also being observed ((*E*)-**1**:**1b** = 1:0.55) (entry 6). Methanol gave 3% of (*E*)-**1** (entry 7) as the only product. Therefore, acetonitrile was found to be the optimal solvent for this transformation and was used in all subsequent studies.



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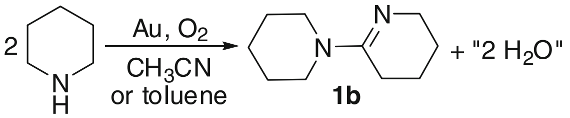

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To gain a more detailed understanding of the reaction, the rate of reaction (Eq. 7) was measured at several piperidine concentrations. As shown in Fig. 1, the rates increased significantly with increasing concentration of amine. The dependence of the rates on amine concentration

Table 1 Gold powder catalyzed reactions of EDA with piperidine and O_2 according to Eq. 7

Entry	Solvent	(*E*)-**1**[a]
1	CH_3CN	94%
2[b]	CH_3CN	6%
3[c]	CH_3CN	N.R.
4	Toluene	82%[d]
5	Toluene	38%[e]
6[f]	THF	17%[g]
7	MeOH	3%
8	$ClCH_2CH_2Cl$	0

0.2 mmol of EDA and 0.6 mmol of piperidine in 5 mL of solvent with 1.00 g of Au powder under ~1.0 atm O_2 for 24 h at 60 °C

[a] Yields were determined by ^{1}H NMR with Ph_3CH as the internal standard

[b] Under ~1.0 atm Ar

[c] No Au catalyst

[d] Imine byproduct **1b** was observed (*E*)-**1**:**1b** = 1:1

[e] At 80 °C, (*E*)-**1**:**1b** = 1:2

[f] For 45 h

[g] (*E*)-**1**:**1b** = 1.0:0.55

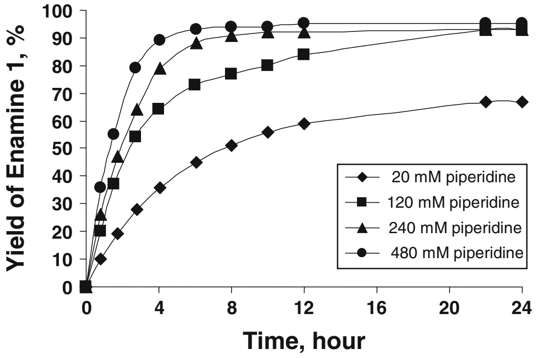
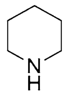
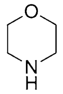
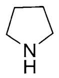
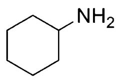
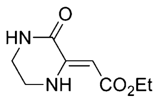


Fig. 1 Formation of enamine as a function of time in the reaction (Eq. 7) of EDA (40 mM) with piperidine in acetonitrile at 60 °C under 1.0 atm of O_2 as catalyzed by 1.0 g of gold powder

is similar to that observed in gold powder-catalyzed reactions of secondary amines with isocyanides [10]. This amine dependence suggests that the rates will also depend on the nature of the amine involved in the reaction, as discussed below.

We were concerned that soluble gold species, such as stabilized nanoparticles or Au(I) and/or Au(III) complexes, may be the active form of the catalyst. In order to test for this possibility, we ran the reaction (Eq. 7) of EDA (0.20 mmol) and piperidine (0.60 mmol) in CH_3CN (5 mL) under 1.0 atm of O_2 in the presence of 1.0 g of gold powder at 60 °C. The gold was in a very active form as it had been used in only two previous reactions after being prepared from $HAuCl_4$ (see "Experimental Section"). Triphenylmethane (0.0447 mmol) was added as a GC standard. After 2.5 h of reaction, the yield of the enamine product (*E*)-**1** was 44%. At that time, 2.5 mL of the reaction solution at 60 °C was removed by syringe and added to an empty tube, which did not contain gold powder. After adding an O_2 atmosphere, the tube was heated to 60 °C for an additional 23 h. GC analysis of the solution showed that no additional (*E*)-**1** was formed, and the amount of unreacted EDA was the same as that observed after being separated from the gold powder. These results showed that no catalytically-active species were present in the solution. Heating at 60 °C of the other 2.5 mL of the original solution, which still contained the gold powder (1.0 g), was continued under an O_2 atmosphere. After 5.5 h, the yield of (*E*)-**1** was 97%. These experiments demonstrate that solid gold, and not a solution-soluble species, is the actual catalyst of the reaction. Similar experiments showed that solid gold powder was the actual catalyst of the reaction of CO, O_2, and primary amines to give ureas [11], the oxidative-dehydrogenation of amines to give imines [13, 14], and the reaction of carbene precursors (diazoalkanes and 3,3-diphenylcyclopropene) to give olefins [25].

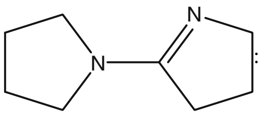
Table 2 Gold powder-catalyzed reactions of EDA with amines and O_2 according to Eq. 6

Entry	Amine	Product	Yield[a]	*E*/*Z*[b]
1		**1**	94%	*E*
2		**2**	82%	*E*
3		**3**	79%	*E*[c]
4	^{i}Pr$_2$NH	**4**	58%	5:1[d]
5	^{n}BuNH$_2$	**5**	89%	*Z*
6	$PhCH_2NH_2$	**6**	78%	1:3[e]
7		**7**	86%	1:12
8	^{t}BuNH$_2$	**8**	85%	1:8
9	$NH_2CH_2CH_2NH_2$		90%	*Z*
10	$PhNH_2$	**9**	N.R.[f]	
11	*p*-$Me_2NC_6H_4NH_2$		N.R.[f]	

0.2 mmol of EDA and 0.6 mmol of amine in 5 mL of CH_3CN with 1.00 g of Au powder at 60 °C under O_2 (~1 atm) for 24 h

[a] Yields were determined by ^1H NMR with Ph_3CH as the internal standard

[b] (*E*,*Z*) isomers were determined by ^1H NMR, NOE and comparison of the data with authentic samples. (*E*/*Z*) ratio is the ratio of the olefinic protons of the (*E*)- and (*Z*)-isomers in ^1H NMR spectra

[c] Imine **3b**  : (*E*)-3 = 0.1:1

[d] Imine **4b** $(CH_3)_2C{=}NCH(CH_3)_2$:(*E*)-4 = 0.2:1

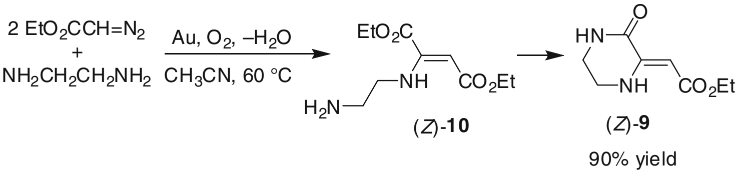
[e] Imine **6b** $PhCH{=}NCH_2Ph$:(*Z*)-6 = 0.25:1

[f] No reaction

3.2 Reactions of Other Diazoalkanes and Amines

Reactions (Eq. 6) of EDA with aliphatic secondary amines (entries 1–4) and primary amines (entries 5–9) in CH_3CN at 60 °C under oxygen using gold powder as the catalyst

(Table 2) provided the corresponding enamines in good to high yields. The cyclic secondary amines, piperidine (entry 1), morpholine (entry 2), and pyrrolidine (entry 3), and primary amines, n-BuNH$_2$ (entry 5), cyclohexylamine (entry 7), t-BuNH$_2$ (entry 8) and $NH_2CH_2CH_2NH_2$ (entry 9), produced enamines in 78–94% yield. The lower yields from pyrrolidine (entry 3), diisopropylamine (entry 4), and benzylamine (entry 6) are due to the competing formation of imines resulting from the gold catalyzed oxidative-dehydrogenation of these amines (Eqs. 1 and 8) [13, 14].



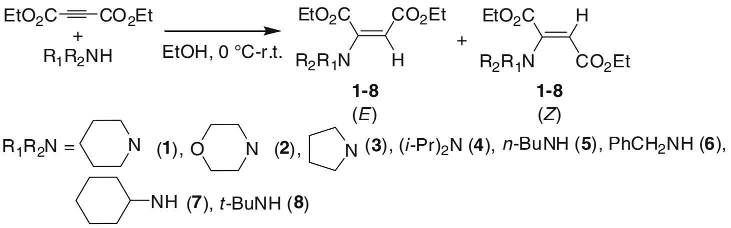
(Z)-**10** (Z)-**9**

90% yield

(9)

No reaction occurred between aniline or p-$Me_2NC_6H_4NH_2$ and EDA (entries 10 and 11), even in the presence of added DABCO or Et_3N base.

Of particular interest are the relative amounts of the E and Z isomers produced from the different amines. Secondary amines give primarily E-isomers (entries 1–4), while primary amines favor Z-isomers (entries 5–9). The cyclic secondary amines produced exclusively E-isomers (entries 1–3), while primary amines n-BuNH$_2$ and $NH_2CH_2CH_2NH_2$ yielded only Z-isomers (entries 5 and 9).



1-8 (E) **1-8** (Z)

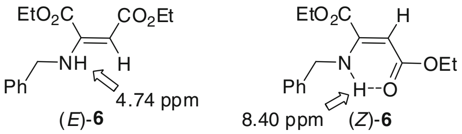
(**1**), (**2**), (**3**), (**4**), (**5**), (**6**), (**7**), (**8**)

(10)

In contrast, diisopropyl amine (entry 4, $E/Z = 5{:}1$), benzylamine (entry 6, $E/Z = 1{:}3$), and t-BuNH$_2$ (entry 8, $E/Z = 1{:}8$) were less stereoselective. In the case of the primary diamine $NH_2CH_2CH_2NH_2$ (entry 9), the formation of product (Z)-**9** presumably resulted from the stereoselective generation of enamine (Z)-**10**, which cyclized to (Z)-**9** (Eq. 9). The ^{1}H NMR spectrum of (Z)-**9** is the same as that reported in the literature [60] for this compound. The (E)-selectivity for the reaction of EDA with secondary amines is very similar to the reactions of dimethyl acetylenedicarboxylate (DMAD) with amines in which the (E)-configuration of the enamine esters was shown to be thermodynamically preferred [56–59]. The dominant (Z)-selectivity for primary amines is presumably due to the formation of a hydrogen bond between the free NH and the carbonyl oxygen as shown in Scheme 1, which was proposed by Iwanami as the reason for the formation of (Z)-enamines from the reactions of DMAD with primary amines [61]. In products obtained from primary amines, the (Z)-enamines show a broad singlet for the NH proton at low field (>8.0 ppm) in the ^{1}H NMR spectrum due to the formation of a hydrogen bond, but the (E)-isomers show the NH proton at around 4.7 ppm.

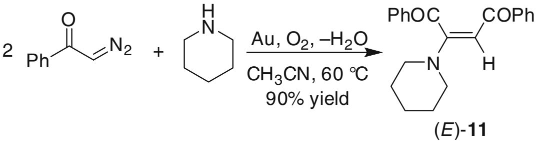
Authentic samples of enamines **1–8** were prepared in essentially quantitative yields from reactions of diethyl acetylenedicarboxylate (DEAD) with amines (Eq. 10) (see Electronic Supplementary Material). The configurations of the (E)- and (Z)-isomers were established by comparison of their ^{1}H NMR spectral data with those of the dimethyl analogs reported by Vernon [58, 59], Dolfini [62], and Saidi [63]. The (E)-enamines show a singlet near 4.7 ppm for the olefinic proton, while the (Z)-isomers show a singlet at about 5.1 ppm.

The reactions of α-diazoacetophenone $PhCOCH{=}N_2$ with amines have been reported to yield N–H insertion products using Cu metal powder as the catalyst (Eq. 5) [48]. We also investigated these reactions with the gold powder catalyst. However, no N–H insertion occurred



(E)-**6** (Z)-**6**

Scheme 1 Effect of hydrogen bonding in the (Z)-isomer on the NH chemical shift under conditions used in our gold metal catalyzed reactions. The reaction of $PhCOCH{=}N_2$ with piperidine provided only enamine (*E*)-**11** in 90% yield after heating 29 h in CH_3CN at 60 °C (Eq. 11); with the primary amine *n*-$BuNH_2$, only the enamine (*Z*)-**12** was obtained in 85% yield under the same conditions (Eq. 12). As in the reactions of EDA, the *E* isomer was obtained with the secondary amine, and the *Z*-isomer was the only product with the primary amine. Heating a mixture of $PhCOCH{=}N_2$ and aniline under the same conditions gave no N–H insertion product or enamine; however, it gave a 30% yield of the olefin product **13** (*cis*/*trans* = 1:3) resulting from the gold catalyzed dimerization of $PhCOCH{=}N_2$ and oxazole product **14** (35% yield) resulting from the reaction of the carbene intermediate with the MeCN solvent (Eq. 13), as reported previously [25].



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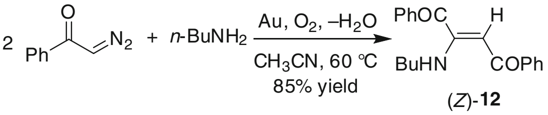

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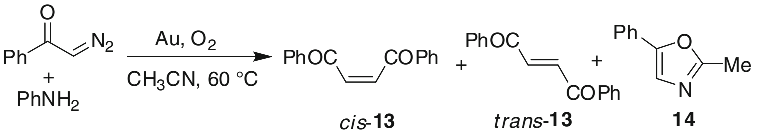
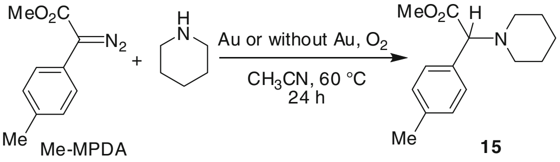


(13)

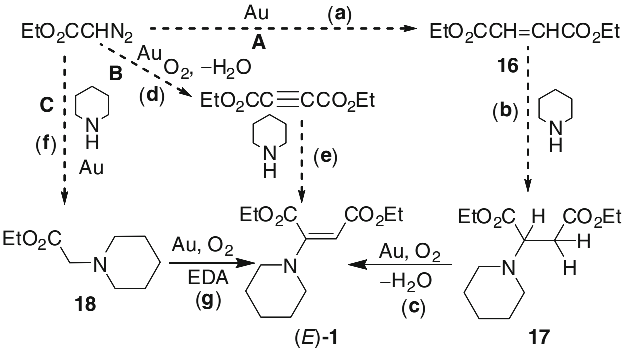
Other diazo compounds were also investigated. The reaction of phenyl diazomethane $PhCH{=}N_2$ with piperidine gave a 70% yield of stilbene $PhCH{=}CHPh$ (*cis*/*trans* 1:1) under the standard conditions; no enamine or N–H insertion products were observed. This yield of stilbene is significantly lower than that (92% yield) obtained in the gold-catalyzed reaction of $PhCH{=}N_2$ in the absence of piperidine [25] under the same conditions. In contrast to the reactions above, methyl (4-methylphenyl)diazoacetate (Me-MPDA) and methyl (4-methoxylphenyl)diazoacetate (MeO-MPDA) react with amines to give N–H insertion products under the same conditions. For example, the reaction of Me-MPDA with piperidine provided a 50% yield of product **15** and some other uncharacterized byproducts (Eq. 14). But this reaction also gave a 66% yield of **15** even in the absence of the gold catalyst under the same conditions. Although this reaction has been reported to be catalyzed by complexes of Ru, Fe, and Cu [33–45], we are not aware of a previous report of the uncatalyzed reaction.



(14)

3.3 Mechanistic Considerations for the Gold-Catalyzed Reactions of Diazoalkanes with Amines and O_2 (Eq. 6)

On the basis of previous studies of gold powder-catalyzed reactions (see "Introduction"), there are three logical mechanisms (Scheme 2) for the formation of enamine (*E*)-**1** from EDA and piperidine. In pathway **A**, the first step (**a**) is the coupling of carbene groups derived from EDA to give olefin **16**, a reaction that is well-established in our previous work [25]. The second step (**b**) is a Michael addition of piperidine to **16** to give **17**; we have shown that this reaction occurs in 100% yield in the *absence* of the gold catalyst under the conditions of reaction (6). The final step (**c**) in pathway **A** is the oxidative-dehydrogenation of **17** to give (*E*)-**1**. Unfortunately, this conversion did *not* occur under the conditions of the reaction, which suggests that **A** is not a likely pathway for reaction (6). In pathway

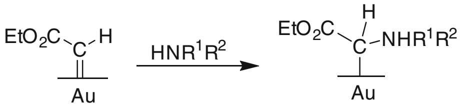


Scheme 2 Plausible mechanisms for gold powder-catalyzed reaction of EDA with piperidine and O_2 (Eq. 6)

B, the oxidative-dehydrogenation of EDA in step (**d**) is followed by amine addition (**e**) to DEAD to give the product. Although the latter reaction (**e**) is well-known as described above (Eq. 10) and in reference [64–69], step (**d**) does not occur as shown in the gold-catalyzed reaction of EDA in the absence of amine; this reaction gives the carbene coupled products (Eq. 2) [25]. Thus, pathway **B** is also unlikely. In pathway **C**, the first step (**f**) involves N–H insertion, which is plausible because of the known insertion reaction (Eq. 14) of Me-MPDA with piperidine. However, the conversion of this product **18** to (*E*)-**1** does not occur under the conditions of the reaction. Thus, none of the pathways, **A**, **B**, or **C**, is consistent with the experimental results.

While it is possible to write other mechanisms for the reaction in Eq. 6, they would be highly speculative. However, trends in the reactivities of different diazoalkanes and amines are consistent with a key step in the mechanism that involves amine attack on a surface carbene (Scheme 3), analogous to reactions of transition metal carbene complexes with amines (Eq. 3). If the amine is not sufficiently nucleophilic, this step is slower than coupling of two carbene groups to form the $EtO_2CCH{=}CHCO_2Et$ isomeric products (Eq. 2). Thus, there is no reaction of EDA with the weakly nucleophilic anilines, $PhNH_2$ and *p*-$Me_2NC_6H_4NH_2$ (Table 2, entries 10 and 11). On the other hand, the more nucleophilic aliphatic amines (Table 2) give enamine products, presumably because their addition to the surface carbene is faster than the coupling of two carbene groups. The tendency of carbene groups to be attacked appears to depend on the presence of an electron-withdrawing group such as $–CO_2Et$ or –C(O)Ph as both EDA and $PhCOCH{=}N_2$ give enamine products with piperidine (Eqs. 6 and 11). On the other hand, the reaction of $PhCH{=}N_2$, lacking an electron-withdrawing group, with piperidine gives none of the enamine but only stilbene (PhHC=CHPh) resulting from coupling of carbene groups and an oxazole resulting from reaction of the carbene with the acetonitrile solvent (Eq. 13).

The reaction of Me-MPDA with piperidine (Eq. 14) is a special case as this reaction occurs even in the absence of the gold catalyst and gives a N–H insertion product, which is not observed in any of the gold-catalyzed reactions.



Scheme 3 Proposed key step in the mechanism for gold powder catalyzed reaction of EDA with amines and O_2 (Eq. 6)

4 Conclusion

The bulk gold-catalyzed reactions of diazoalkanes with amines and O_2 described in this paper show that the gold metal need not be nanosized in order to be a highly active catalyst. These reactions represent a fundamentally new type of reaction that is catalyzed by bulk gold. Moreover, the enamine products are different than the N–H insertion products that are obtained when the same reactants are combined in the presence of transition metal complex or copper metal catalysts. Formation of the enamine products is facilitated by electron-withdrawing groups ($–CO_2Et$ and –C(O)Ph) in the diazoalkane and by nucleophilic amines. A mechanism involving amine attack on a surface-adsorbed carbene group, e.g.,:$C(H)(CO_2Et)$, is consistent with these trends. If the amine attack is slow, other products resulting from coupling of the carbene groups or oxidative-dehydrogenation of the amines are formed. These fundamental studies using a gold powder catalyst suggest that bulk gold supported on a high surface area material could be used as a practical catalyst of these reactions. No other catalysts of these reactions have been previously reported.

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