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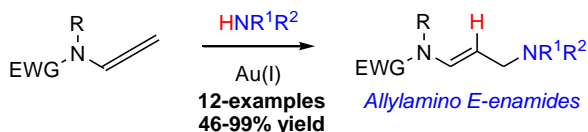
An Intermolecular Hydroamination of Allenamides Catalysed by Cationic Au(I) Salts

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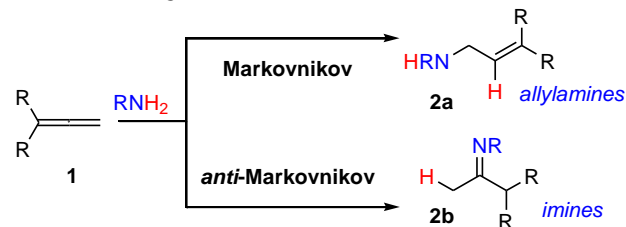


An intermolecular hydroamination of allenamides has been achieved under mild Au(I) catalysis conditions delivering allylamino *E*-enamides stereoselectively and in high yield. The reaction is made possible *via* a convenient method for conjugated *N*-acyliminium formation.

The addition of the N-H bond over alkene and alkyne π -systems, the hydroamination transformation, represents a powerful method for the introduction of the amine functionality.¹ Such transformations give access to a range of valuable nitrogen containing building blocks such as amines, imines and enamines. Within this group of reactions the intermolecular hydroamination of allenes has become increasingly important due to the regiochemical factors in such transformations. Allenes (**1**) can undergo either Markovnikov or *anti*-Markovnikov addition, giving rise to allylamines (**2a**) or imines (**2b**) (Scheme 1). This first group of substrates, allylamines, are vital synthetic building blocks since they are contained within a number of important biological systems and are key intermediates in organic synthesis.²

A number of transition metal approaches towards the hydroamination of allenes have been reported, including the use of Zr (*anti*-Markovnikov), Hg (Markovnikov), Pt (Markovnikov) and Pd (Markovnikov) salts.³ Additional to

these transition metals, Au salts have proved to particularly attractive in hydroamination reactions due to their low toxicity and increased stability to moisture and air.⁴ Consequently, a number of groups have utilised Au salts in these transformation to great effect.^{1b,5}



SCHEME 1. The hydroamination of allenes.

Recently, we reported⁶ the first intermolecular hydroarylation of allenamides⁷ with electron rich aromatics using an Au(I) catalyst to give the corresponding enamides. Enamides⁸ are a class substrates that have become particularly topical due to their use in the construction of heterocycles, chiral amines and their presence in a number of natural product frameworks.⁹ This transformation was high yielding

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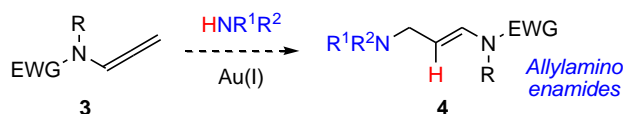
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for most substrates and gave exclusively the *E*-enamide. Importantly, unlike many of the methods¹⁰ for enamide preparation, the reaction required no exclusion of air and moisture and the reaction was extremely facile.

While there are reported methods for the Au catalysed intermolecular hydroamination of allenes to give allyl amines within the literature,⁵ methods for the intermolecular hydroamination of allenamides remains untouched to our knowledge. Whereas the hydroamination of allenes delivers synthetically useful allylamines, the intermolecular Markovnikov addition of an N-H bond over an allenamide **3** would deliver an allylamino enamide **4**, a substrate that would contain both an allyl amine and an enamide within the one synthetic framework (Scheme 2). Therefore, in this communication we would like to share our results of the first intermolecular hydroamination of allenamides using aniline derivatives under our Au(I) catalytic conditions.

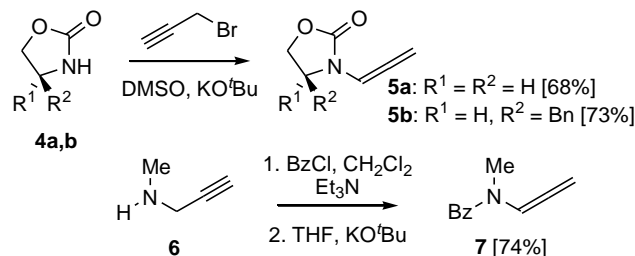


SCHEME 2. The proposed hydroamination of allenamides.

The allenamides used for this study are shown below in Scheme 3. Cyclic allenamides **5a** and **5b** were synthesised using an adapted method of Heaney,¹¹ and the acyclic allenamide **7** was synthesised *via* initial amide formation followed by base catalysed rearrangement.¹²

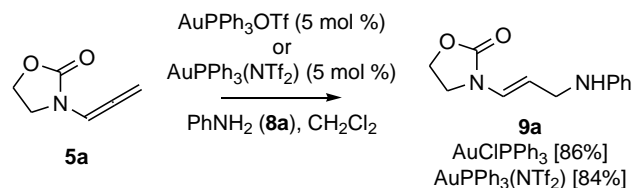
Our starting point would be the conditions used for our hydroarylation protocol.⁶ Therefore a solution of allenamide **5a** (1.00 equiv.) and aniline **8a** (1.05 equiv.) in CH₂Cl₂ was treated with a catalytic amount (5 mol%) of cationic Au(I)PPh₃OTf generated from AuCIPPh₃ and AgOTf at room temperature (Scheme 4). To our delight the hydroaminated

product **9a** was isolated in 86% yield after chromatography. The enamide was obtained exclusively as the *E*-isomer, and the addition of the N-H bond to the activated allenamide gave the Markovnikov product.



SCHEME 3. Preparation of allenamides **5a,b** and **7**.

A comparable yield of 84% was also obtained using 5 mol% of the Au(I) complex, AuPPh₃(NTf₂). The stereochemistry of the *E*-enamide double bond was supported by a combination of ¹H and ¹³C NMR, IR spectroscopy (coupling constant 14.0 Hz and 1673 cm⁻¹) and single crystal X-ray analysis.¹³



SCHEME 4. Hydroamination of allenamide **5a**.

The applicability of this protocol was then further explored, the results of which are summarised in Table 1. Haloanilines **8b** and **8f** successfully added to the allenamide giving the enamides **9b** and **9f** in good yield (entries 1 and 5). Introduction of an electron withdrawing ethyl ester *para* to the NH₂ gave the enamide **9c** in a moderate 61% yield (entry 2), while a nitro group at the *ortho* position was tolerated and gave the enamide **9d** quantitatively (entry 3). 2,5-Dimethyl aniline **8e** and 3-methoxyaniline **8g** both successfully added to the activated allenamide to give the hydroaminated products **9e** and **9g**, respectively (entries 4 and 6). Unfortunately, pentafluoroaniline **8h** failed to add to the activated allenamides, presumably due to its low nucleophilicity (entry 7). Finally, *N*-methyl aniline **8i** readily participated in the hydroamination reaction giving the *N*-methyl enamide **9i** in near quantitative yield (entry 8).

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(13) Crystal data for **9a**: C₁₂H₁₄N₂O₂, M = 218.25, monoclinic, *I*2/a; *a* = 16.015(3) Å, *b* = 5.4583(9) Å, *c* = 25.143(5) Å, β = 99.848(2)°, *V* = 2165.5(7) Å³, *D*_{calc} = 1.339 g/cm⁻³, μ_{max}(Mo-Kα) = 0.093 mm⁻¹; λ = 0.71073 Å, *T* = 150(2) K; 12077 total reflections, 3283 unique data (*R*_{int} = 0.0277); Solved by direct methods and refined on *F*² values to give *R*₁ = 0.0428. See supporting information for further details.

TABLE 1. Substrate scope for the Au(I) catalysed hydroamination of allenamide **5a**.^a

Entry	Substrate	Product ^b	Yield [%] ^c
1			79
2			91
3			99
4			83
5			98
6			61
7		No reaction	0
8			98

^aSee experimental section for procedure; ^bdata for all new compounds is contained within the supplementary information; ^cIsolated yields

The hydroamination reaction was also performed with chiral and acyclic allenamides and the results are shown below in **Table 2**.

TABLE 2. Variation of the allenamide in the Au(I) catalysed hydroamination reaction.^a

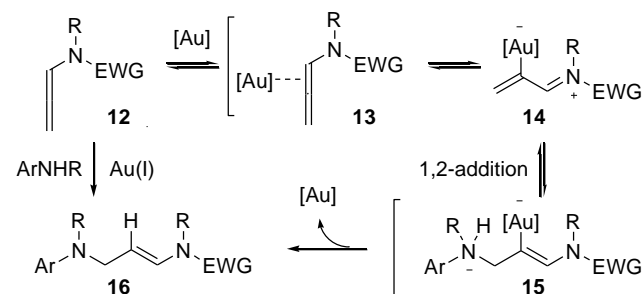
Entry	Substrate	Aniline	Product ^b	Yield [%] ^c
1		8a		79
2		8f		91
3		8f		46
4		8g		47

^aSee experimental section for procedure; ^bdata for all new compounds is contained within the supplementary information; ^cIsolated yields

Chiral allenamide **5b** successfully underwent hydroamination with both aniline **8a** and 2-iodoaniline **8f**

giving the chiral enamides **10a** and **10b**, respectively. No epimerization was observed, but slightly reduced yields as compared to the achiral allenamide **5a** was seen (entries 1 and 2). The acyclic allenamide **7** also underwent hydroamination with anilines **8f** and **8g**. A crude ¹H NMR of enamides **11a** and **11b** indicated full conversion to the desired products, however the isolated yields were modest at best and we have attributed this to product degradation during purification.

A mechanistic rationale for this transformation is outlined in **Scheme 5**.



SCHEME 5. Mechanistic rationale for the hydroamination reaction.

We believe that the cationic Au(I) salt activates the allenamide **12** to give an conjugated *N*-acyl iminium intermediate species **14**. This can undergo either 1,2- or 2,3-addition by a suitable nucleophile. In the case at hand the aniline derivatives undergo 1,2-addition giving **15** which can then undergo protodemetalation to yield the observed *E*-enamide **16**.

In summary, we have disclosed an Au(I) catalysed protocol for the intermolecular hydroamination of allenamides. The reaction is facile, high yielding and stereoselectively gives the *E*-enamide products. The products of this reaction, allylamino enamides, have the potential to be valuable building blocks in organic synthesis since they contain two vital functionalities, allyl amines and enamides, within one framework. The chemistry of this building block, the mechanistic insights and the addition of other nucleophilic species to the Au activated conjugated *N*-acyl iminium species are currently being studied in our group and will be reported on in due course.

Experimental section¹⁴

Representative hydroamination method with allenamide 5a. To a solution of the allenamide **5a** (63 mg, 1.05 equiv., 0.50 mmol) in dichloromethane (3.00 mL) at room temperature was added the aniline derivative (1.05 equiv.) followed by AuPPh₃OTf (from AuClPPh₃ [12.40 mg, 5.00 mol%, 0.025 mmol] and AgOTf [6.60 mg, 5 mol%, 0.025 mmol]) and the resultant solution stirred for up to 1h at room temperature (monitored by tlc). The resultant reaction mixture was then filtered through a plug of Celite[®] and the crude mixture purified by column chromatography (ethyl acetate/petroleum ether mixture as indicated). **9a** was obtained

(14) Full experimental details and compound data are available in the supporting information

as a pale yellow solid ($R_f = 0.42$) (93 mg, 86 %, MP 89 – 91 °C); [Found (ES): MNa^+ , $C_{12}H_{14}N_2O_2$, 241.0944, requires MNa^+ 241.0953]; IR (solution, $CHCl_3$) 3441, 3012, 1759, 1673, 1602, 1504, 1482, 1417, 1250 cm^{-1} ; 1H NMR (400 MHz; $CDCl_3$) δ 7.18 (t, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 14.0$ Hz, 1H), 6.72 (t, $J = 7.6$ Hz, 1H), 6.62 (d, $J = 7.6$ Hz, 2H), 4.96 (dt, $J = 6.4, 14.0$ Hz, 1H), 4.42 (dd, $J = 8.0, 9.2$ Hz, 2H), 3.80 (d, $J = 6.4$ Hz, 2H), 3.73 (bs, 1H), 3.69 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.3(C), 147.8(C), 129.3(CH), 126.4(CH), 117.8(CH), 113.1(CH), 107.7(CH), 62.2(CH₂), 43.8(CH₂), 42.5(CH).

Representative hydroamination method with allenamide

5b. To a solution of the allenamide **5b** (50 mg, 1.00 equiv., 0.232 mmol) in dichloromethane (2.00 mL) at room temperature was added the aniline derivative (1.05 equiv.) followed by $AuPPh_3OTf$ (from $AuCIPPh_3$ [5.80 mg, 5.00 mol%, 0.012 mmol] and $AgOTf$ [3.00 mg, 5 mol%, 0.012 mmol]) and the resultant solution stirred for up to 1h at room temperature (monitored by tlc). The resultant reaction mixture was then filtered through a plug of Celite® and the crude mixture purified by column chromatography (ethyl acetate/petroleum ether mixture as indicated). **10a** was obtained as a colourless oil ($R_f = 0.5$) (48 mg, 68%); $[\alpha]_D^{20} = 26.0$ (c 1.00, $CHCl_3$) [Found (ES): MNa^+ , $C_{19}H_{20}N_2O_2$, found 331.1413, requires MNa^+ 331.1422]; IR (solution, $CHCl_3$) 3014, 2926, 1755, 1670, 1503, 1413, 1310, 1238, 1206 cm^{-1} ; 1H NMR (400 MHz; $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.20 (t, $J = 8.0$ Hz, 2H), 7.15 – 7.13 (m, 2H), 6.84 (d, $J = 14.4$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.66 (d, $J = 8.4$ Hz, 2H), 5.22 (dt, $J = 6.4, 14.4$ Hz, 1H), 4.27 – 4.17 (m, 3H), 3.87 – 3.83 (m, 2H), 3.21 – 3.18 (m, 1H), 2.81 – 2.76 (m, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.8(C), 147.8(C), 135.2(C), 129.3(CH), 129.3(CH), 129.0(CH), 127.4(CH), 125.3(CH), 117.9(CH),

113.2(CH), 108.3(CH), 66.7(CH₂), 55.0(CH), 44.2(CH₂), 36.3(CH₂).

Representative hydroamination method with allenamide

7. To a solution of the allenamide **7** (50 mg, 1.00 equiv., 0.289 mmol) in dichloromethane (3.00 mL) at room temperature was added the aniline derivative (1.05 equiv.) followed by $AuPPh_3OTf$ (from $AuCIPPh_3$ [7.20 mg, 5.00 mol%, 0.014 mmol] and $AgOTf$ [3.70 mg, 5 mol%, 0.014 mmol]) and the resultant solution stirred for up to 1h at room temperature (monitored by tlc). The resultant reaction mixture was then filtered through a plug of Celite® and the crude mixture purified by column chromatography (ethyl acetate/petroleum ether mixture as indicated). **11a** was obtained as a yellow oil ($R_f = 0.35$) (52 mg, 46%); [Found (ES): MNa^+ , $C_{17}H_{17}IN_2O$, found 331.415.0271, requires MNa^+ 415.0283]; IR (solution, $CHCl_3$) 3441, 3011, 1638, 1590, 1506, 1389, 1069 cm^{-1} ; 1H NMR (400 MHz; $CDCl_3$) (*mixture of rotamers*) δ 7.64 (d, $J = 7.6$ Hz, 1H), 7.49 – 7.40 (m, 5H), 7.20 (t, $J = 7.2$ Hz, 1H), 6.78 (bs, 1H), 6.50 (bs, 1H), 6.48 – 6.44 (m, 1H), 5.16 (bs, 1H), 4.17 (bs, 1H), 3.77 – 3.75 (m, 2H), 3.27 (bs, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) (*mixture of rotamers*) δ 170.9(C), 146.4(C), 139.1(CH), 135.7(C), 133.0(CH), 129.4(CH), 128.7(CH), 128.0(CH), 119.0(CH), 110.8(CH), 105.7(CH), 85.7(C), 44.1(CH₂), 30.4(CH₃).

Acknowledgments. The author thanks Loughborough University for financial support.

Supporting Information Available. Experimental procedures, 1H and ^{13}C NMR spectra, characterization for **9a-9i**, **10a, b**, **11a, b** and the crystallographic data for **9a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.