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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Selective Carbon-Carbon Bond Formation : Terpenylations of Amines Involving Hydrogen Transfers

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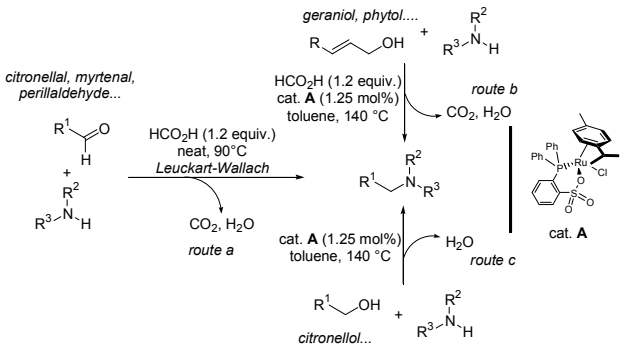
Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

The well-defined ruthenium(II) complex A featuring a phosphine sulfonate chelate promotes the introduction of terpene motives onto cyclic saturated amines through hydrogen "auto"transfers without side alkene reduction. These eco-friendly transformations enable the production of diverse *N*- and *C*- terpenoid alkaloids with only water and carbon dioxide as benign side products.

Introduction

The broad family of terpenes and their oxygenated terpenoid partners resulting from the assembly of isoprene units represent a class of secondary metabolites arising from biomass and isolated from plants and fungi.[1] Besides their historical application in perfume, fragrances,[1a,2] or medicines,[3] these compounds have also attracted considerable interest as raw materials for fine chemicals,[2,4] agrochemicals,[5] and as renewable ressource for rubber and polymerization chemistry.[6] Arising from the attachment of terpene moieties to various non terpenic organic molecules such as indoles, coumarins, hybrid isoprenoids are a special class of molecules which revealed high biological activity, presumably due to their increased affinity to biological membranes.[7] Similarly, terpene alkaloids ranging from prenylated to steroidal alkaloids, have a broad range of biological properties.[8,9] Another interest of « aza-terpenes » results in the quaternization of the amines allowing the access of diverse amphiphiles with potential industrial properties as surfactants or ionic liquids.[10] Synthetic preparation of *N*-terpenylated amines with simple terpenes usually involved telomerization, hydroamination and related reactions.[4b,11,12] Geranylation and prenylation of amines with allylic alcohol derivatives such as prenol, linalool, geraniol via catalytic nucleophilic substitution are also documented.[13] Reductive amination of terpenaldehydes represent another important approach.[14] However, even if the preparation of C(2)- and C(3)-prenylated indole derivatives to access isoprenoids are reported,[15] straightforward accesses of novel *C*-terpenylated saturated amines minimizing the steps and wastes are still unknown. Recently, we demonstrated that well-defined ruthenium(II) and iridium(III) containing phosphine sulfonate as chelating ligand allowed the C(3)-H functionalization of amines with aldehydes via an oxidant free dehydrogenation.[16] This reactivity involving hydrogen autotransfers took advantage of the ability of the in situ generated metal hydride species resulting from the dehydrogenation of amines to reduce the iminium intermediates formed upon condensation with aldehydes. Herein, we report on the preparation of various *N*-terpenylated amines and their application in catalytic hydrogen autotransfer reactions for the access to diverse amines containing two or three terpene moieties via C-H functionalization.



Scheme 1 Preparation of tertiary amines via *N*-terpenylation.

Results and Discussion

Initially, the preparation of the *N*-terpenylated alkaloids **3** (Figure 1) was easily achieved by using three different pathways. Starting from aldehydes such as citronellal, myrtenal, safranal with secondary cyclic amines **2**, *N*-terpenylation occurred under neat reaction condition using the so-called Leuckart-Wallach reaction in up to 95% isolated yield (Scheme 1 – route a).[17,18] From allylic alcohols such as geraniol and phytol, *N*-alkylated amines **3** were obtained via a tandem isomerization-reductive amination sequence in the presence of **cat. A** and formic acid acting as hydrogen donor through hydrogen transfer processes by using our previously described methodology (Scheme 1 – route b).[19] Finally the borrowing hydrogen methodology starting from alcohol such as citronellol led to the formation of *N*-geranylated amines in up to 63% isolated yield (Scheme 1 – route c).[20] Overview of the *N*-terpenylated amines **3** is outlined in Figure 1. With the freshly prepared *N*-terpenylated amines **3** in hand, we

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data for **cat. D** and compounds **3**, **4**, **5**. See DOI: 10.1039/b000000x/

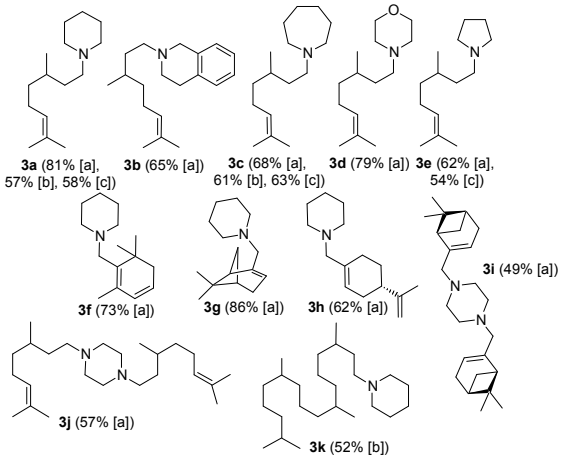
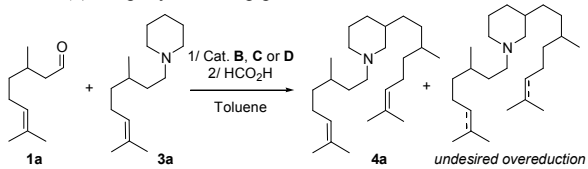


Figure 1 Overview of prepared *N*-terpenylated amines **3** via hydrogen transfers (preparation route indicated in brackets).

next explored the reactivity of the racemic *N*-geranylated piperidine **3a** with citronellal **1a** towards β-geranylation in the presence of the ruthenium complex **cat. B**, the iridium precatalyst **cat. C** featuring phosphine sulfonate chelate and **cat. D** containing a pyridone chelate obtained by treatment of $[Ru(p\text{-cymene})Cl_2]_2$ with the deprotonated hydroxyquinoline (see S I) (Figure 2). Thus, alkylated piperidine **3a** was first reacted with citronellal **1a** in the presence of a catalyst and CSA as additive at 150 °C for 16 h, and after cooling formic acid was added as a reducing agent at the last stage of the procedure to ensure complete reduction of the unsaturated intermediates at 150 °C for 2 h (Table 1). Under these reaction conditions, the amines act both as nucleophile through the formation of enamine intermediates and as hydrogen donor for the generation of metal hydride species enabling the reduction of the iminium species. Noteworthy, piperidines **4a** were obtained as a mixture of eight stereoisomers due to the presence of three stereogenic carbon centers in the final molecule including the formation of one of them during the β-alkylation step. When the β-geranylation was attempted under our initial reaction conditions with iridium

Table 1 *C(3)*-Terpenylation of piperidine **3a** with citronellal **1a**[a]



Entry	catalyst	HCO_2H (n equiv.)	CSA (mol %)	Selectivity[b]	Conversion (Yield)[c]
1	**Cat. B**	2.0	7	73	92(62)
2[d]	**Cat. B**	1.5	4	90	91(80)
3	**Cat. C**	1.5	4	58	89
4[e]	**Cat. C**	1.0	4	65	92
5	**Cat. D**	1.5	4	90	83(67)

[a] All reactions were carried out at 0.135 M concentration in toluene at 150 °C for 16 h, 3 h under an inert atmosphere of argon with **1a**/**3a**/[Cat] in 1/1.1/0.03 molar ratio and CSA as additive. [b] Selectivity calculated by GC analysis toward **4a** and side products arising from over-reduction. [c] Conversion based on GC analysis. Number in parenthesis is isolated yield. [d] Second step at 130 °C. [e] Second step at 100 °C.

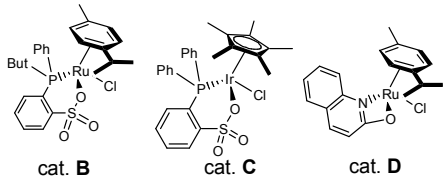
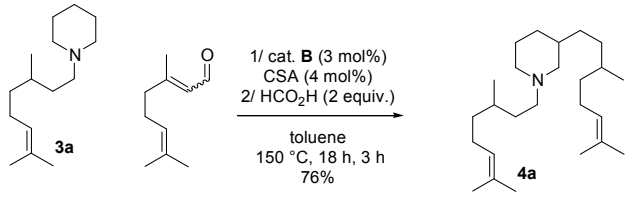


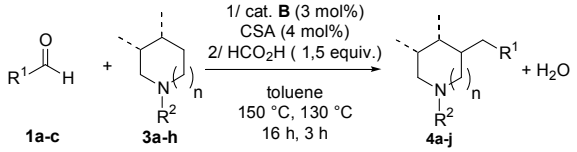
Figure 2 Evaluated precatalysts.

cat. C, the expected product **4a** was formed but large amounts of side products resulting from the over reduction of the C=C insaturations via hydrogen transfer processes were observed (entry 3). Attempts with lower amount of formic acid and reduced reaction temperature were unsuccessful highlighting the low chemoselectivity for this transformation (entry 4). On the other hand, the application of the ruthenium(II) **cat. D** was more fruitful affording the expected digeranylated piperidines **4a** in a 67% isolated yield (entry 5). The transformation in the presence of the ruthenium **cat. B** occurred with a better chemoselectivity and led to 62% isolated yield (entry 1). Finally, the best result was obtained by using 1.5 equiv. of formic acid and a reduced temperature of 130 °C at the last stage yielding 80% of the isolated digeranylated piperidine **4a** (entry 2). With the *N*-terpenylated cyclic amines prepared from Figure 1 and under our best reaction conditions, the substrate diversity toward ruthenium-catalyzed *C*-terpenylation was explored with various biosourced terpenaldehydes (Table 2). In most cases the reaction went smoothly affording the expected diterpenylated amines in moderate to good yields. Reaction of piperidine **3a**, tetrahydroisoquinoline **3b** and pyrrolidine **3e** derivatives with racemic citronellal **1a** led to the formation of stereoisomeric mixtures of digeranylated amines in 62-80% isolated yield (entries 1-3). *N*-Geranylated morpholine **3d** was also compatible affording **4d** in 69% isolated yield (entry 4). The presence of stereoisomers in these previous compounds prevented the accurate determination of the diastereoselectivity during C-H functionalization and in order to tackle this issue we decided to start from the achiral amine **3f** derived from safranal. It was noted that a good 72% isolated yield was obtained but most significantly even at these high temperatures a promising 72% diastereoisomeric excess was observed (entry 5). Noteworthy, NMR analyses revealed that no C=C isomerization occurred on the dienic structure. α,β-Unsaturated aldehydes have never been examined during β-alkylation of amines and interestingly, during the transformation of the enantiopure amine **3g** with (-)-myrtenal, a moderate diastereoisomeric excess of 62% was obtained but importantly using 1.5 equivalent of formic acid highlighted that the former conjugated double bond was not hydrogenated affording amine **4h** in 57% isolated yield (entry 8). The same trend was observed with perillaldehyde and both C=C bonds remained intact giving amines **4g**, **4i** and **4j** in up to 71% isolated yield (entries 7, 9 and 10). In contrast, the reaction of **3a** with an

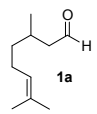
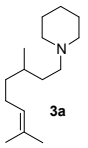
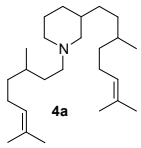
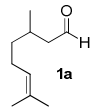
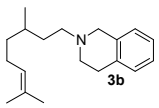
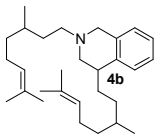
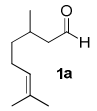
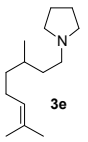
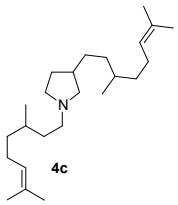
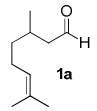
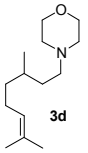
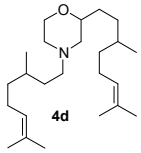
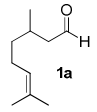
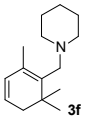
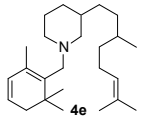
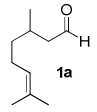
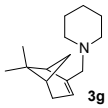
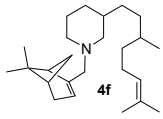
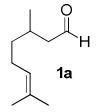
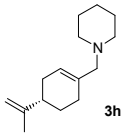
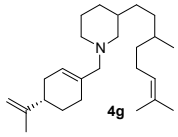
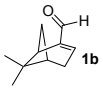
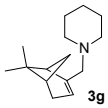
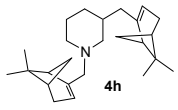
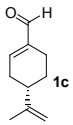
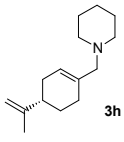
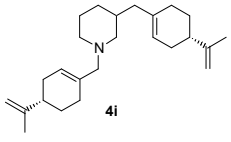
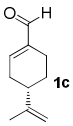
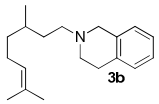
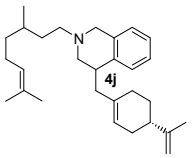


Scheme 2 Geranylation with citrals

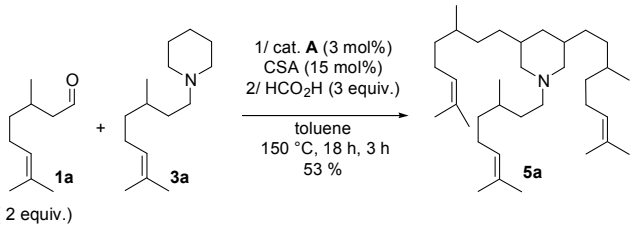
Table 2 Ruthenium-catalyzed β-terpenylation of amines **3**[a]



1a-c **3a-h** **4a-j**

Entry	Terpene **1**	Amine **2**	Product **3**	d.e[c].	Yield[d]
1				-[b]	80
2				-[b]	68
3				-[b]	62
4				-[b]	69
5				72	72
6				-[b]	56
7				-[b]	60
8				62	57
9				5	71
10				-[b]	67

[a] All reactions were carried out at 0.135 M concentration at 150 °C for 16 h under an inert atmosphere of argon with **1**/**3**/[Ru] in 1/1.1/0.03 molar ratio. [b] stereoisomeric mixture. [c] diastereomeric excess. [d] isolated yield.



Scheme 3 Trigeranylated piperidines **5a**

acyclic α,β-unsaturated aldehyde such as citrals led to the major formation of the diterpenylated amines **4a** resulting from the reduction of the former conjugated C=C enal bond whereas the distal unsaturation remained intact (Scheme 2). At this stage, piperazine derivatives **3i** and **3j** didn't react likely due to the difficult deprotonation of the iminium intermediates preventing enamine formation. Finally, another approach to highlight the interest of our methodology in synthesis consisted in the formation of triterpenylated amines arising from functionalization at the two C(3)-position of the *N*-terpenylated amine **3a**. We demonstrated that the chemoselective formation of the trigeranylated piperidine **5a** was possible in the presence of 2 equivalents of aldehyde **1a** simply by increasing the amount of Brønsted acid (CSA) from 4 to 15 mol % leading to the formation of the lipophilic amine **5a** in 53% isolated yield (Scheme 3).

Conclusion

In summary, the oxidant free dehydrogenative C-H bond functionalization of *N*-terpenylated cyclic amines was successfully performed with various terpenaldehydes without side alkene reduction in the presence arene ruthenium(II) catalyst containing a chelating phosphine sulfonate. Starting from enantiopure or non chiral amines **3**, this method, enabled promising diastereoselective formation of disusbtituted amines with water and carbon dioxide as the only side products. Amine quaternization of these raw biosourced materials followed by postfunctionalization via cross metathesis of the remaining unsaturations would afford the access to valuable amphiphiles.[10,21]

Aknowledgements

The authors thank the financial support from the Ministry of Higher Education and Research of Algeria for a PNE fellowship to Z.S.. Thanks are also due to CEFIPRA/IFCPAR (IFC/A/3805-2/2008/1720) for a grant to B.S.

Experimental

Procedure for the preparation of amines 4:

To a stirred solution of amine **3** (1.1 equiv.) in 1.5 mL of toluene was added aldehyde **2** (1 equiv., 0.2 mmol). Subsequently D-(+)-camphor sulfonic acid (3 mol %) and **cat. B** (3 mol %) were added and then the sealed Schlenk tube was stirred at 150 °C (oil bath temperature) for 16 h. After 16 h, the reaction mixture was cooled down and then HCOOH (1.5 equiv.) was added and stirring was continued at 130 °C for 3 h. The crude mixture was directly taken for GC analysis and purified by column chromatography (Et_2O/PE/Et_3N) to afford the βC-alkylated amines **4**.

3-(3,7-dimethyloct-6-en-1-yl)-1-((2,6,6-trimethylcyclohexa-1,3-dien-1-yl)methyl)piperidine 4e

Compound **4e** was prepared according to the general procedure for the preparation of amines **4** after purification through column chromatography (Et_2O/PE/Et_3N: 1/9/0.025) in 72% yield with a 72% diastereoisomeric excess. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71-5.64 (m, 2H), 5.02 (t, 1H, *J*= 7.0 Hz), 2.86 (s, 2H), 2.68-2.63 (m, 2H), 1.92-1.74 (m, 6H), 1.69 (s, 3H), 1.61(s, 3H), 1.53 (s, 3H), 1.36-1.20 (m, 8H), 1.13-1.02 (m, 4H), 0.98 (s, 6H), 0.77 (d, 3H, *J*= 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.6, 129.9, 128.8, 126.5, 124.1, 124.0, 59.4, 59.2, 55.5, 52.8, 39.6, 36.0, 36.0, 35.5, 33.1, 32.5, 31.6, 30.8, 30.4, 30.2, 29.9, 28.6, 25.1, 24.7, 24.5, 18.5, 17.4, 16.6, HRMS calculated for $C_{25}H_{44}N^+$: $[M+H]^+$ 358.34738 , found $[M+H]^+$ 358.3474.

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