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Hydroaminomethylation of eugenol with di-n-butylamine catalyzed by rhodium complexes: Bringing light on the promoting effect of Brönsted acids

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ABSTRACT

The hydroaminomethylation of eugenol with di-n-butylamine was performed employing a bis[(1,5-cyclooctadiene)(μ-methoxy)rhodium(I)] as pre-catalyst. In the absence of phosphines, the catalyst was efficient in the process, but the regioselectivity for amines was poor. For phosphine-promoted catalyst, the chemoselectivity at the hydroformylation step improved, but the hydrogenation of enamine intermediates was hampered. The regioselectivity within the class of amines was surprisingly high (>96%) for the linear product. The addition of triflic acid (10–20 mol%) improved significantly the efficiency of HAM. Employing the 2,2′-bis((diphenylphosphino)methyl)-1,1′-binaphthyl as ancillary and triflic acid as a promoter, the linear product was obtained in up to 93% yield.

1. Introduction

The hydroaminomethylation of olefins (HAM) is a three-step reaction consisting of the hydroformylation of an olefin, the condensation of the formed aldehyde with an added primary or secondary amine, and the catalytic hydrogenation of the resulting imine/enamine to yield the corresponding amine. The last two steps are closely related as the amine condensation is reversible and the hydrogenation step withdraws the imine/enamine from the equilibrium, driving the reaction to completion. This tandem transformation [1] is exemplified in Scheme 1 for the HAM of eugenol (**1**) with di-n-butylamine.

Although known for a long time [2], only recently has HAM gained importance in the synthesis of more complex molecules [3], such as pharmaceuticals and other biologically active substances [4–9]. The use of special ligands such as diphosphines [10], diphosphites [7], xanthene-based dipyrrolylphosphines [11], and tetradentated phosphorus ligands [12] has allowed good selectivity control associated with high activity. The development of biphasic systems, in which the catalyst is dissolved in water [13], ionic liquids [14], or multiphase thermophilic systems [15], has allowed for the easier catalyst recycling, which favors industrial applications. The advances in this synthetically efficient process have been recently reviewed [16].

Our group is involved in the preparation of useful or potentially useful chemicals employing transition metal complex catalyzed reactions applied to natural products that can be obtained in kiloton scale through sustainable methods [17–20]. We have recently reported the HAM of various monoterpenes to obtain amines, which have potential bioactivity [21]. Herein we report the HAM of eugenol (**1**) with di-n-butylamine (Scheme 1) to obtain three new amines. Despite the potential bioactivity of the products, to the best of our knowledge, it is the first time that HAM of arylpropenes of natural sources is described.

2. Experimental

2.1. General procedure

Eugenol, di-n-butylamine, triphenylphosphine, sulfuric acid, para-toluenesulfonic acid, and trifluoromethanesulfonic acid were purchased from Aldrich. 2,2′-bis((Diphenylphosphino)methyl)-1,1′-binaphthyl (NAPHOS) was kindly donated by Prof. B. Hanson (Virginiatech-USA). Toluene was refluxed over sodium/benzophenone for six hours and distilled under argon. [Rh(cod)(μ-OMe)]$_2$ was synthesized according to literature procedure [22].

2.2. Catalytic runs

The pre-catalyst [Rh(cod)(μ-OMe)]$_2$ (5.0×10^{-3} mmol), the phosphorus ancillary (if any) and a PTFE-covered magnetic stirring bar were placed in a stainless steel bomb, which was closed and purged with three cycles of vacuum and argon. In a Schlenk tube, a solution was prepared by adding toluene (30 mL), eugenol (10 mmol), di-n-butylamine (10 mmol) and then the acid (if any). The solution was transferred under inert atmosphere to the bomb,

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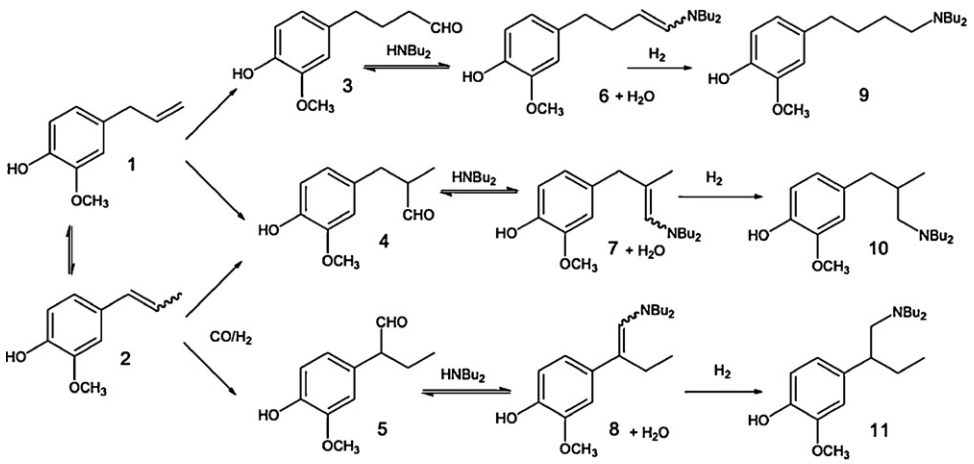

Scheme 1.

which was pressurized with carbon monoxide (10–20 atm) and then with hydrogen (to 40–80 atm). The bomb was placed in a pre-heated silicone bath over magnetic stirring. Liquid samples were taken periodically through a dip tube.

2.3. Product analysis

The products were quantitatively analyzed by gas chromatography (GC) using a Shimadzu GC2010 instrument equipped with a split/splitless injection port and flame ionization detector, fitted with a Restek Rtx-5 capillary column (30 m × 0.25 mm × 0.25 μm). Conversion and product distribution were determined by GC based on the reacted eugenol. Qualitative analysis was made by GC coupled with mass spectrometry in a Shimadzu GC2010/QP2010-plus instrument fitted with a Restek Rtx-5 MS capillary column (30 m × 0.25 mm × 0.25 μm), operating at 70 eV. The main products were isolated by column chromatography and analyzed by and ^{1}H, ^{13}C, DEPT-NMR (Bruker Avance DRX 200, TMS, $CDCl_3$).

2.4. Spectroscopic data

9: Mass spectrometry: (*m*/*z*/rel.int.): 307/5.0 (M+); 264/100; 168/15; 142/90; 100/50; 44/20 ^{13}C NMR: 14.02, 20.71, 26.05, 28.52, 29.66, 35.46, 53.49, 53.59, 55.78, 110.98, 114.23, 120.79, 134.33, 143.67, 146.43. ^{1}H NMR: 0.90 (t, 6H, CH_3, ^{3}J = 7.0 Hz); 1.55–1.23 (m, 12H, CH_2); 2.54–2.42 (m, 8H, CH_2); 3.86 (s, 3H, CH_3); 6.65 (d, 2H, Ar:CH, ^{3}J = 7.6 Hz); 6.81 (d, 1H, Ar:CH, ^{3}J = 7.6 Hz).

10: Mass spectrometry: (*m*/*z*/rel.int.): 307/5 (M+); 142/100; 100/58; 44/11. ^{13}C NMR: 13.90; 18.05, 20.57, 29.62; 34.03, 35.32; 53.31, 54.29; 55.50, 110.95; 114.44; 120.55, 134.00, 143.74; 146.59. ^{1}H NMR: 1.11 (t, 9H, CH_3, ^{3}J = 6.8 Hz); 1.68–1.47 (m, 8H, CH_2); 1.99 (m, 1H, CH); 2.74–2.55 (m, 8H, CH_2); 4.02 (s, 3H, CH_3); 6.84 (d, 2H, Ar:CH, ^{3}J = 8.4 Hz); 6.99 (d, 1H, Ar:CH, ^{3}J = 7.6 Hz).

11: Mass spectrometry: (*m*/*z*/rel.int.): 264/5; 142/100; 100/55; 44/30. ^{13}C NMR: 12.07; 14.00, 20.53, 27.58, 28.47, 45.71, 53.94, 55.87; 60.66; 110.42; 114.15, 120.34, 136.42, 143.86; 146.35. ^{1}H NMR: 0.75 (m, 3H, CH_3, ^{3}J = 7.4 Hz); 0.86 (m, 6H, CH_3, ^{3}J = 7.2 Hz); 1.42–1.21 (m, 10H, CH_2); 2.49–2.39 (m, 4H, CH_2); 2.62–2.56 (m, 3H,CH, CH_2); 3.88 (s, 3H, CH_3); 6.65 (d, 2H, Ar:CH, ^{3}J = 7.6 Hz); 6.84 (d, 1H, Ar:CH, ^{3}J = 7.8 Hz).

3. Results and discussion

The hydroaminomethylation (HAM) of eugenol (**1**) with di-n-butylamine led to three isomeric amines (**9**–**11**), as depicted in Scheme 1. Depending on the reaction conditions, the intermediate aldehydes (**3**–**5**) and enamines (**6**–**8**) were also observed in the reaction solution. In Table 1 the results for HAM of **1** employing different catalytic systems and reaction conditions are presented.

In entries 1 and 2 and Fig. 1 the unpromoted and the triphenylphosphine-promoted rhodium catalysts are compared at 100 °C. For the unpromoted system (entry 1 and Fig. 1(a)), the reaction was quite efficient as the substrate was completely converted into products after 2 h. Nevertheless, the chemoselectivity was poor as ca. 20% of the isomeric olefin **2** was formed. Under these conditions, **2** was also converted into products, as **11** could be exclusively formed from **2**. After 24 h, 90% of the reactant was converted into

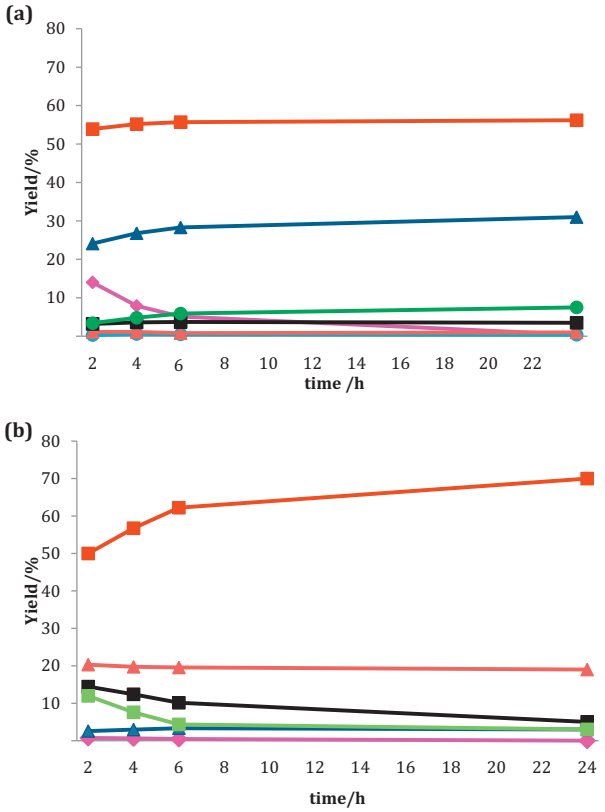

Fig. 1. Hydroaminomethylation of eugenol: (a) unpromoted system and (b) PPh_3-promoted system (2 3 4 5 6 9 10 11). For conditions, see Table 1.

Table 1
Hydroaminomethylation of eugenol (**1**) with di-n-butylamine: ligand effect.[a]

Entry	Ligand	P/Rh[b]	Conv. (%)	Product distribution (%)				Regioselectivity (%)[c]		
				2	Aldehydes	Enamines	Amines	**9**	**10**	**11**
1	None	0	100[d]	4	1	0	90	61	33	6
2	PPh_3	2	100	0	24	3	73	96	4	0
3	PPh_3	10	100	0	32	10	58	94	5	1
4	NAPHOS	2	34	3	34	56	7	>99	0	0
5[e]	NAPHOS	2	100	10	21	5	64	97	3	0

[a] Conditions: **1** (10 mmol); di-n-butylamine (10 mmol); $[Rh(cod)(\mu\text{-}OMe)]_2$ (5.0×10^{-3} mmol), toluene (30 mL), 4.0 MPa (CO:H_2 = 1:3), 100 °C, 24 h. For products, the value "zero" means not observed or <0.5%.
[b] Phosphorus/rhodium atomic ratio.
[c] Related to the sum of amines (**9** + **10** + **11**).
[d] 5% of hydrogenation of substrate.
[e] 120 °C.

amines, but the regioselectivity was poor and ca. 5% of the hydrogenation product (not shown in Scheme 1) was also formed.

In order to reach a better selectivity control, two equivalents of PPh_3 were added to the system (entry 2 and Fig. 1(b)). For the PPh_3-promoted system at 100 °C, the chemoselectivity at the hydroformylation step increased, as the isomerization and hydrogenation products were drastically reduced. After 2 h, 50% of the linear amine **9** was formed, but the rate of the enamine hydrogenation slowed down in comparison to the unpromoted system. Both the aldehydes **3** and **4** and the enamine **6** were observed in significant amounts after two hours of reaction. The latter was slowly converted into **9** and the equilibrium **3**/**6** was shifted to the product. It is noteworthy that, although 20% of the branched aldehyde **4** was formed, no significant amount of the branched enamine **7** was observed (Fig. 1(b)), due to the fact that the equilibrium **4**/**7** was shifted to the reactant. As the equilibrium concentration of **7** was low and so was its rate of hydrogenation, the amine **10** was formed at a very low rate. Although regioselectivity is defined at the hydroformylation step (irreversible), it was possible to obtain a high regioselectivity *within the class of amines* for the linear product **9** due to a kinetic resolution in the steps of amine condensation/enamine hydrogenation. Thus, with this protocol it is possible to obtain the linear amine in a high regioselectivity (96%) employing the cheap PPh_3 ligand, which is produced worldwide in a multi-ton scale.

In Table 1, entry 3, the PPh_3/Rh is 10. Under these conditions the enamine hydrogenation was even less efficient, as the enamine amount increased from 3% to 10% (c.f. entries 2 and 3). At a higher concentration of PPh_3, the rhodium species containing one or no phosphorus ligand must be reduced and these species, which have comparatively lower electron density at the metal center, seem to play an important role in the enamine hydrogenation step [21,23].

In order to improve the regioselectivity for the linear product at the hydroformylation step, we employed the chelating diphosphine 2,2′-bis((diphenylphosphino)methyl)-1,1′-binaphthyl (NAPHOS) as ancillary. In a previous work [24], we successfully employed this ligand to favor the regioselectivity for linear products in the hydroformylation of arylpropenes, such as eugenol, eugenol methyl ether and safrole. Nevertheless, under hydroaminomethylation conditions at 100 °C and P/Rh molar ratio of two (Table 1, entry 4), the system presented a poor performance: after 24 h only 34% of the substrate was converted and only 7% of amines were formed. With this chelating diphosphine, the amount of the rhodium species containing one or no phosphorus atom bound to the metal is reduced and the ones containing two phosphorus atoms are too electron rich to carry out efficiently the enamine hydrogenation under the conditions employed. At 120 °C (entry 5), the HAM of eugenol employing the Rh/NAPHOS system showed to be more efficient, but still only 64% of the substrate was converted into amines after 24 h.

In previous works [6,11,13,25], it has been reported that the addition of acids is beneficial for the hydroaminomethylation, although the reasons remain unknown. In order to get some insight into this matter, we performed a comparative study employing strong acids of the same nature, but with different pK_a and coordination capacities. The results are presented in Table 2. For the PPh_3-promoted system at 120 °C in the absence of acids (entry 6), the reaction was quite efficient, as 83% of the product was converted into amines with a high regioselectivity within the amine class. Surprisingly, under the same reaction conditions, but with the addition of sulfuric acid (10 mol% with respect to **1**) made the system less active both at the hydroformylation step and, especially, in the enamine hydrogenation step. Only 2% of amines were formed after 24 h, in spite of the fact that 86% of the substrate was converted into

Table 2
Hydroaminomethylation of eugenol (**1**) with di-n-butylamine: effect of added acid.[a]

Entry	Ligand	P/Rh[b]	Acid	Temp. (°C)	Conv. (%)	Product distribution (%)				Regioselectivity (%)[c]		
						2	Aldehydes	Enamines	Amines	**9**	**10**	**11**
6	PPh_3	2	None	120	100	0	17	0	83	96	4	0
7	PPh_3	2	H_2SO_4[d]	120	86	13	76	9	2	94	6	0
8	PPh_3	2	HOTs[d]	120	100	0	23	0	75	89	11	0
9	PPh_3	2	HOTf[d]	120	100	1	11	0	88	84	14	2
10	NAPHOS	2	HOTf[e]	100	100	5	9	0	86	99	1	0
11	NAPHOS	20	HOTf[e]	100	100	2	5	0	93	99	1	0
12	NAPHOS	40	HOTf[e]	100	100	2	3	0	95	98	2	0

[a] Conditions: **1** (10 mmol); di-n-butylamine (10 mmol); $[Rh(cod)(\mu\text{-}OMe)]_2$ (5.0×10^{-3} mmol), toluene (30 mL), 4.0 MPa (CO:H_2 = 1:3), 24 h. For products, the value "zero" means not observed or <0.5%.
[b] Phosphorus/rhodium atomic ratio.
[c] Related to the sum of amines (**9** + **10** + **11**).
[d] 1.0 mmol.
[e] 2.0 mmol.

products (entry 7). The acid-catalyzed trimerization of the aldehydes, which is detrimental to the enamine formation, must also be considered as an explanation for the lack in conversion of aldehydes to enamines in entry 7. Comparing the system in the absence of acid (entry 6) with the one in the presence of para-toluenesulfonic acid (entry 8), it is possible to observed that, after 24 h, less of amines were formed, but the proportion of **10** increased. The latter observation suggests that the system became more efficient for the enamine hydrogenation, while the former observation suggests that the acid hampers the amine condensation step. Employing the considerably stronger trifluoromethanesulfonic acid (HOTf) under the same reaction conditions (entry 9) the HAM became considerably more efficient as 88% of amines were formed in 24 h. The branched enamine was also converted at a higher rate, as **10** corresponded to 14% of the amine products after 24 h.

The promoting effect of the acid on HAM has been explained in at least two manners [6,13]. Employing the strong tetrafluoroboric acid (HBF_4) as a promoter, Routaboul et al. [6] suggested that the role of the acid would be to protonate the intermediate imine or enamine, as the corresponding imminium or enaminium salt could be hydrogenated more easily. Behr et al. [13] employed the ammonium salts of acids with different strengths instead of the amine counterparts. The authors suggested that the effect of the acid could be related to the formation of cationic rhodium species that are more efficient for the imine/enamine hydrogenation. Indeed, cationic rhodium complexes are efficient catalyst to hydrogenate C—C double-bonds in molecules containing other coordinating groups [26], such as enamines. In a stoichiometric study, Crozet et al. [27] demonstrated the interplay of cationic and neutral rhodium species under conditions relevant for the HAM. When para-toluenesulfonic acid was added to a neutral rhodium species, it was readily converted into a cationic one. Nevertheless, when piperidinium para-toluenesulfonate was employed in place of HOTs, the formation of the cationic species did not occur even after 24 h.

The strength of the acids employed in this work varies significantly, as the pK_{a1} for sulfuric acid is −3, for HOTs is −2.8, and for HOTf is −14. On one hand, as we used 5 to 10-fold excess of di-n-butylamine, a leveling effect is expected and, at the beginning of the reaction, the strongest acid must be the di-n-butylammonium formed due to the protonation of the di-n-butylamine by the acids. On the other hand, the counter-anions have different coordination abilities (SO_4^{2-} > OTs^- > OTf^-) and the enamine hydrogenation ability of the systems follows the reversal of this order. Even that the ammonium ion is acidic enough to promote the formation of cationic complexes, in the presence of coordinating counter-ion, a neutral complex would be immediately formed. Only strong acids, which generate a non-coordinating ion by hydrogen loss, can produce a stable cationic complex. This observation can be interpreted as favoring the hypothesis that the ammonium ion is acidic enough to promote the formation of cationic complexes, which would efficiently hydrogenate the enamines, provided the counter-ion is a non-coordinating one. Nevertheless, it does not rule out the hypothesis that the effect of the acid is to protonate the intermediate enamine (or imine) favoring its hydrogenation through the enaminium (or iminium) salt.

Actually, the HAM can be performed using the ammonium salt of the amine counterpart [13], and it is likely that both effects are important for the HAM. Regardless of the explanation, trifluoromethanesulfonic acid (triflic acid) proved to be an excellent promoter for the HAM of eugenol.

Thus, we decided to test NAPHOS in the presence of HOTf as this ligand was successfully used in the HAM of dodecene with dimethylamine to form highly linear fatty amines in the presence of HBF_4 [25]. We tested the system with different amounts of NAPHOS in the presence of HOTf (20 mol% in relation to the substrate) as shown in entries 10–13. Under these conditions the HAM of eugenol with di-n-butylamine was highly efficient and the linear product was formed in up to 99% selectivity. The increase in regioselectivity with the increase in NAPHOS concentration was already observed previously [25] and the effect was attributed to the entrapment of rhodium species without phosphorus ligands that are less regioselective. An alternative explanation is that in such conditions the phosphorus atoms of the ancillaries are partially protonated, which may explain the need for a larger P/Rh ratio to keep good selectivity. Indeed surprising is the fact that the enamine hydrogenation seems to be more efficient at higher NAPHOS concentrations, as in the absence of the acid the opposite behavior was observed. This fact suggests that, in the presence of strong acid bearing non-coordinating anion such as HOTf, the more efficient catalyst for enamine hydrogenation contains electron-donating ligands. This behavior is exactly the opposite of the one observed for systems unpromoted by acids [23]. Finally, in entry 12, we demonstrate that by employing the Rh/NAPHOS/HOTf system, eugenol could be converted into the linear amine **9** in nearly quantitative yield.

4. Concluding remarks

The hydroaminomethylation of eugenol, a bio-renewable substrate available from essential oils of various plants, was performed for the first time. Di-n-butylamine was used as amine counterpart. Three novel amines (**9–11**) were obtained in high yields, with their relative amounts depending on the catalyst and the reaction conditions. The reaction was highly selective to the linear amine **9**, which was produced in up to 93% yield, by the appropriate choice of the ancillary ligand, its amount and the acid additive. Three strong acids of the same nature, but with different pK_a and coordination ability of the counter-ion have been tested and the latter feature has showed to be critical: the less coordinating is the counter-ion, the more efficient is the process. Triflic acid, which is more stable than the previously reported HBF_4, proved to be an excellent promoter for the hydroaminomethylation of eugenol catalyzed by rhodium complexes in the presence of phosphines as ancillaries.

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