

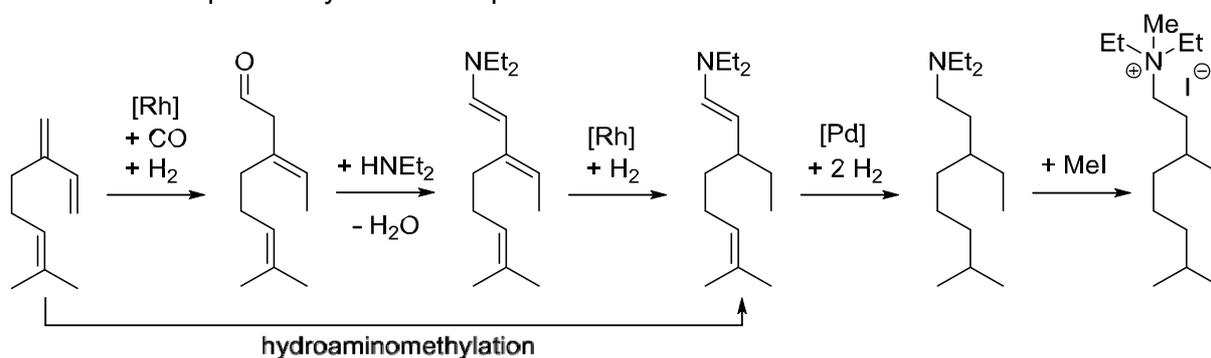
Hydroaminomethylation of 1,3-Dienes – Surfactant Precursors on Basis of Renewable Raw Materials

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Abstract

One major target of modern industrial chemistry is the utilization of renewable feedstocks to improve the sustainability of chemical reactions. In this regard, the development of homogeneously catalysed conversions of readily available renewables into valuable products in a selective and atom economic manner, is getting more and more important. Especially in the introduction of nitrogen, homogenous catalysis has its advantages over heterogeneous catalysis, particularly in terms of high activity and selectivity. Different reactions have already been developed for C-N-linking, like hydroamination, telomerisation or reductive amination. A really interesting and efficient way to obtain primary, secondary or tertiary amines is the use of hydroaminomethylation (HAM), a tandem reaction under syngas pressure.^[1] While the implementation of *n*-alkenes in HAM is an established reaction, the use of 1,3-dienes is rather challenging.^[2]

Now we present the synthesis of a tertiary amine from industrially available, renewable 1,3-diene β -myrcene by selective Rh-catalysed hydroaminomethylation with diethylamine for the first time. The auto-tandem catalytic HAM of myrcene leads to an unsaturated tertiary amine with high regioselectivities of 97% and good yields of 70%. Furthermore, an unprecedented high TOF ($739 \text{ mol} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$) in the hydroformylation step of the diene was observed. Side reactions, like aldol condensation or hydrogenation of the substrate could be suppressed by the right choice of reaction parameters. Additionally the products could be converted into quaternary amine compounds that showed surface active behaviour.^[3]



[1] D. Crozet, M. Urrutigoity, P. Kalck, *ChemCatChem* **2011**, 3, 1102–1118.

[2] A. Behr, S. Reyer, V. Manz, *Chem. Ing. Tech.* **2012**, 84, 108–113.

[3] T. A. Faßbach, T. Gaide, M. Terhorst, A. Behr, A. J. Vorholt, *ChemCatChem* **2017**, 8, 1359-1362.