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REACTION OF TERTIARY ALLYLIC AMINES WITH BUTADIENE CATALYZED BY PALLADIUM[1]

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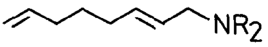
Summary: Tertiary allylic amines react with butadiene in the presence of palladium(0) with cleavage of the carbon-nitrogen bond of the allylic amine and formation of the unsaturated tertiary amine 4.

In the course of our studies of nickel-catalyzed additions of secondary amines to butadiene,[2] we found that, in addition to the main products 1 and 2, small amounts of co-oligomers consisting of one amine and four butadiene units are formed when the reaction mixtures are allowed to stand for several days with an excess of butadiene. By using a palladium(0)-catalyst the yield and the selectivity of this co-oligomerization reaction can be improved. Furthermore, the same products are obtained from butadiene and pre-formed octadienylamine 1.



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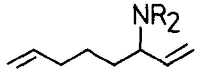

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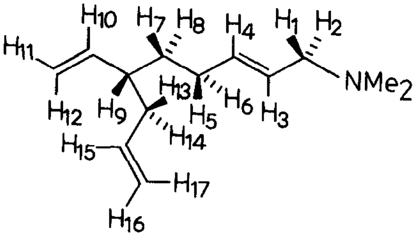
This prompted us to study the palladium(0)-catalyzed reaction of butadiene with other simpler allylic amines. Reaction of N,N-dimethylallylamine (3) (5 mmol) with butadiene (20 mmol) in the presence of bis(triphenylphosphine)palladium(II) chloride (0.1 mmol) and triethylaluminium (0.5 mmol) in toluene (2 ml) gives an unexpected product, N,N-dimethyl-N-6-vinyl-2,8-nonadienylamine (4), along with ca 5% of compound 1. The optimum yield (81% as determined by GLC with dodecane as an internal standard) is obtained after 20 h at 20° followed by 3 h at 60°. Compound 4, as a 93/7 mixture of the *trans* and *cis* isomers, was purified by preparative gas chromatography using a 19 mm x 3 m column of 20% Apiezon L + 10% KOH on Chromosorb W-AW. Higher oligomers, of unknown structure, are formed using a large excess of butadiene and prolonged reactions times (GC-MS evidence).

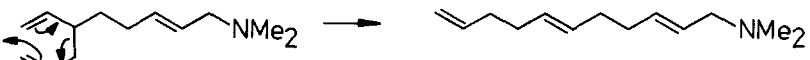
The structure of compound 4[3] was established by NMR spectroscopy. The following data were obtained:



^{1}H-NMR ($CDCl_3$)[4]: δ 1.2-1.6 (H_7 and H_8, m), 1.9-2.2 (H_5, H_6, H_9, H_{13} and H_{14}, m), 2.20 (6H, s), 2.84 (H_1 and H_2, d, $J_{1,3} = J_{2,3} = 5.37$ Hz), 4.9-5.1 (H_{11}, H_{12}, H_{16} and H_{17}, m), 5.47 and 5.56 (H_4 and H_3 respectively, AB-part of an ABM_2X_2-spectrum with $J_{3,4} = 15.4$, $J_{4,5} = J_{4,6} = 5.5$ Hz), 5.6 (H_{10},m) and 5.76 (H_{15}, ddt, $J_{13,15} = J_{14,15} = 7.0$, $J_{15,16} = 11.0$ and $J_{15,17} = 16.4$ Hz). Irradiation of the allylic protons gave rise to an AB-spectrum for H_7 and H_8 with δ 1.32 and 1.48 and $J_{7,8} = 13$ Hz. A singlet at δ 2.22 and a doublet at δ 2.91 probably originate from the *cis* isomer of 3.

^{13}C-NMR ($CDCl_3$)[4]: 29.8(t), 33.8(t), 39.4(t), 43.1(d), 45.1(q), 62.0(t), 114.5(t), 115.7(t), 127.6 (d), 133.8(d), 136.9(d) and 142.3(d) (the multiplicities were determined by off-resonance decoupling).

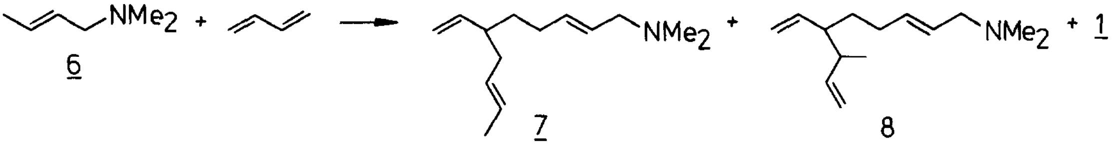
Further evidence for the structure of compound 4 follows from its tendency to undergo a Cope-rearrangement to give the isomer 5 (80% after 1 h at 250°C in a sealed tube).

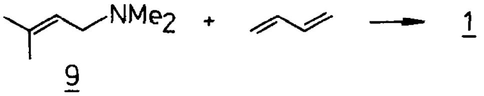


4 5

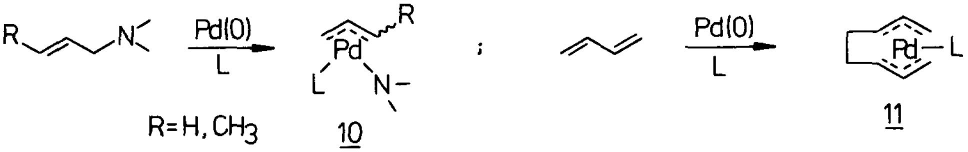
The choice of catalyst is important. Use of tetrakis(triphenylphosphine)palladium(0)[5] in place of the *in situ*-formed palladium(0) gives only 5% of compound 4 along with 15% of compound 1. The presence of a Lewis acid has been shown to be beneficial for both nickel- and palladium-catalyzed reactions of dienes with nucleophiles.[1,6] Indeed, the addition of triethylaluminium results in formation of compound 4 (50%) together with compound 1 (15%), whereas addition of boron trifluoride etherate gives only compound 1 (40%). Use of sodium borohydride in place of triethylaluminium as a reducing agent similarly affords only the octadienylamine (70%).

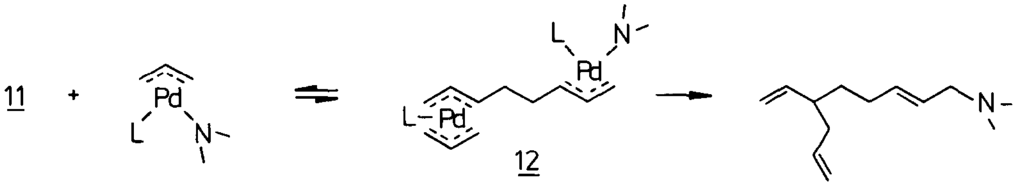
In the palladium-catalyzed reaction of butadiene with N,N-dimethylcrotylamine (6) approximately equal amounts of the two isomers 7 and 8 are formed in a total yield of about 30%. The main product is, however, the octadienylamine 1. Reaction of butadiene with the allylic amine 9 results in exclusive formation of compound 1 (52%).





It has previously been reported[7,8] that allylamine is disproportionated by palladium(0) to give di- and triallylamine and ammonia. These reactions and the reaction reported here probably involve the oxidative addition of the allylamines to palladium with formation of 10. It is well established that butadiene reacts with palladium(0) in the presence of various ligands to give the bis-π-allyl complex 11.[9] The following, tentative, mechanism explains the formation of the products, although other possibilities remain, e.g. direct attack of the allylamine on complex 11. Complexes analogous to 12 have in fact been isolated[10] and it has been suggested that they are formed *via* the complex 11.





The octadienylamine 1 is formed by the addition of a proton instead of an allylic group to C-6 of the butadiene dimer. The source of this hydrogen, as well as the fate of the lost allylic residue, is unknown. In the reaction of the crotylamine 6, β-elimination from complex 10 ($R=CH_3$) with formation of a palladium hydride may take place, followed by reductive elimination of dimethylamine. Reaction of dimethylamine with butadiene would give 1.

Palladium-catalyzed reactions of other allylic substrates with butadiene are presently under investigation.

ACKNOWLEDGEMENTS

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