Allylic Rearrangements During the Rhodium-catalysed Reactions of 2-Allyloxybenzylamines and 2-(*N*-Allyl-*N*-benzylamino)benzylamine

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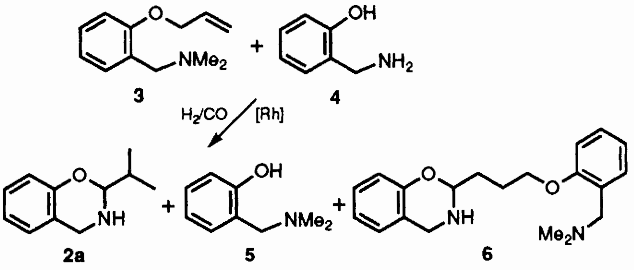
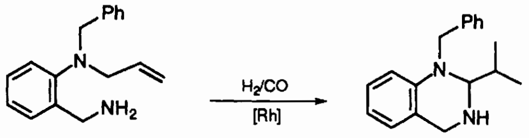
Reactions of 2-allyloxybenzylamines with H_2/CO in the presence of rhodium catalysts give 1,3-benzoxazines *via* a reaction which involves allylic cleavage and carbonylation as demonstrated by crossover experiments.

Rhodium catalysed reactions of some 2-allyloxybenzylamines **1** gave very high isolated yields of substituted 1,3-benzoxazines **2**. Reaction of 2-allyloxybenzylamine **1a** gave 2-isopropyl-3,4-dihydro-1,3-benzoxazine **2a** in 90% isolated yield and the ^1H and ^{13}C NMR spectra of the total reaction mixture showed no evidence for the presence of other compounds (Table 1). An authentic sample of **2a** was prepared by condensation of 2-hydroxybenzylamine with 2-methylpropanal in the presence of molecular sieves.[1]

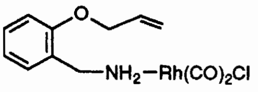
Introduction of a 5-bromo substituent into the aryl ring **1b** also gave a quantitative yield of oxazine **2b**. However, a 3-methoxy substituent gave only polymeric material. Methyl substitution at either end of the allyl moiety (**1d**, **1e**) gave the same product (**2d**, **2e**). This result suggested to us that the products arise *via* a mechanism which involves cleavage of the allyl moiety followed by regioselective carbonylation at the internal carbon atom (Scheme 1).

Support for this mechanism came from a reaction of 2-allyloxy-*N*,*N*-dimethylbenzylamine **3** with $H_2/CO/[Rh]$ in the presence of 2-hydroxybenzylamine **4** which gave the oxazine **2a** together with 2-hydroxy-*N*,*N*-dimethylbenzylamine, and the oxazine **6**. In the absence of 2-hydroxybenzylamine **4**, reaction of **3** gave an equimolar mixture of the deallylated material **5** and the linear aldehyde resulting from terminal hydroformylation of **3**. This aldehyde presumably condenses with **4** in the above sequence leading to the oxazine **6**.





7 **8**



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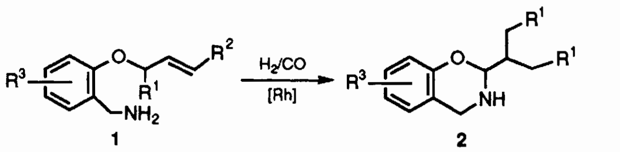
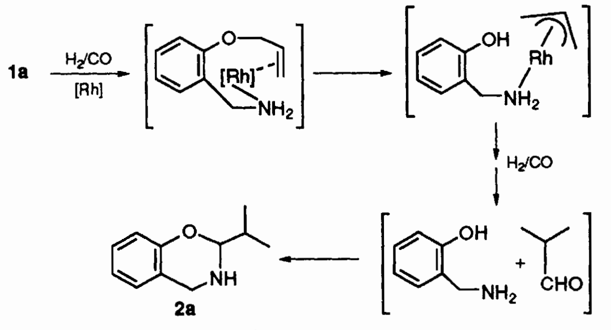


1 **2**

Table 1 Reactions of 2-allyloxybenzylamines **1** with H_2/CO[a]

Substituents	R^1	R^2	R^3	Yield of **2** (%)
a	H	H	H	90
b	H	H	5-Br	90
c	H	H	3-MeO	—[b]
d	Me	H	H	70
e	H	Me	H	90

[a] Reactions were carried out with alkene, $[Rh(OAc)_2]_2$, and PPh_3 (200 : 1 : 4) or alkene and $HRh(CO)(PPh_3)_3$ (200 : 1) for 20 h at 40–60 °C, typically using 3 mmol of alkene in ethyl acetate or benzene (10 ml) and 1 : 1 molar mixture of H_2/CO (2.76 MPa). Yields of material are after distillation. [b] Polymeric material only.



Scheme 1

Allylic migration in metal catalysed reactions has been reported recently during palladium catalysed alkylation reactions[2] and in rhodium catalysed silylaminocarbonylations.[3] Precedents for the regioselective carbonylation of the allyl residue on the central carbon cannot be found but nucleophilic substitution at the central carbon of a π-allylplatinum complex has been reported.[4]

An analogous rearrangement/carbonylation has also been demonstrated in the rhodium catalysed reaction of the nitrogen analogue **7** which gave the quinazoline derivative **8** in 80–90% yield (NMR) together with a small amount of an unidentified compound.

A rhodium complex **9** of **1a** has been prepared following the method of Krafft[5] but attempts to induce rearrangement to a π-allylrhodium has so far not been successful.

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