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Mg and Zn Mediated Allylation of Imines with Allyl Bromide

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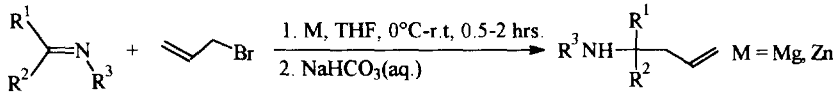
Abstract: Both aldimines and ketimines are allylated under simple Barbier-type conditions using allyl bromide and commercial magnesium foil or zinc dust in tetrahydrofuran at room temperature.

Addition of allylic organometallic species to the imine function and its derivatives constitutes a potentially valuable method for the preparation of homoallylamines.[1a] Significant advances in the Barbier-type imine allylation have been developed in recent years.[2] The metals being used include In,[2a] $CrCl_2/BF_3 \cdot OEt_2$,[2b] Ta, Bi/Bu_4NBr,[2c] $Al/TiCl_4$(cat.),[2d] Al, $Zn/PbCl_2$,[2e] and $Al/PbBr_2$(cat.)/ $BF_3 \cdot OEt_2$,[2f] and the imines are mainly limited to aryl aldimines due to the low reactivity of other imines. On the other hand, the most reactive readily-made allylic organometallic reagents such as allyllithium,[3a] -magnesium,[3b] and -zinc[3c] allylate only the imines derived from nonenolizable or α-alkyl substituted aliphatic aldehydes.[1a,4]

While zinc[1b,5] and magnesium[6] allow the use of very mild conditions for allylation of carbonyl compounds to produce homoallylic alcohols, the use of zinc in Barbier-type allylation of imines in certain cases has received only scant attention,[7] and the use of magnesium for an efficient allylation of imines has never been reported. We report herein that both aldimines and ketimines are efficiently allylated by magnesium foil or commercial zinc powder without any activation under simple Barbier-type conditions (eq.1).

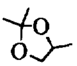


(eq.1

Representative results are shown in **Table 1**. Imines derived either from aromatic, aliphatic, heteroaryl, and α, ß-unsaturated aldehydes (entry 1-10) or from aromatic and aliphatic ketones (entry 11, 12) all reacted with the *in situ* generated allylic metallic species in the usual way to produce the corresponding homoallylamines in excellent yields. These results contrast with that of the reported Barbier-type allylation system[2] and the readily-made allylic organometallic reagents[3,4] in terms of high efficiency and less limitation for the substrates. It seems that the stronger basicity of the allylic magnesium or zinc bromide could overcome the less electrophilicity of the C=N bond; Meanwhile the high efficiency indicated that as soon as the Grignard reagents were generated they were instantaneously trapped by the electrophilic C=N bond[3a] and the very low concentration of the allylic anion made it possible to avoid those side reactions of imines[8] as well as the coupling and dimerization reactions involved in the preparation of the allylmagnesium bromide reagents.[9]

In the presence of equal mole of (-) - sparteine (entry 3), the Zn system only gave the racemic addition product, while the Mg system failed to work in the same condition; When the chiral imines were used (entry 8-

Table 1. Reaction of Imines with Allyl Bromide and Metals[a]

entry	R^1	R^2	R^3	Yield, %[b]	
				Mg	Zn
1	Ph	H	Ph	99	97
2	Ph	H	Bn	92	95
3	p-ClC_6H_4	H	Bn	98 (0)[c]	98 (75)[c]
4	*trans*-PhCH=CH	H	Bn	82	91
5	2-Furyl	H	Bn	90	93
6		H	Ph	86	90
7	*i*-Butyl	H	Bn	85	92
8	Ph	H	(S)-PhCH(Me)	84 (1/1)[d]	86 (1/1)[d]
9	p-$MeOC_6H_4$	H	(S)-PhCH(Me)	93 (1/1.5) 80 (1/2.5)[e]	88 (1/1) 77 (1/1)[e]
10	o-$MeOC_6H_4$	H	(R)-PhCH(Me)	85 (2.5/1)	84 (2/1)
11	Ph	CH_3	Bn	98	98
12	Et	CH_3	Bn	94	83

[a] All reactions were run in 0.5-mmol scale (imine/allyl bromide/Mg or Zn = 1/1.1/1.2), monitored by TLC and worked up as usual. All products showed consistent physical and spectroscopic properties. [b] Isolated yields. [c] Run at -78 °C - rt in the presence of 1 equiv. of sparteine. [d] Ratios in parenthesis represent the diastereoisomeric ratios obtained by 300 MHz ^{1}H-NMR spectra. The configuration was not determined. [e] Run at -78 °C - rt.

10), the diastereoselectivity was disappointed and accorded with that of the readily prepared Grignard reagent.[4]

In summary, the present two systems provide novel procedures for allylation of imines with advantages of their generality, mild reaction condition, simple manipulation, efficiency and economy.

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