CHEMISTRY LETTERS, pp. 673-674, 1987.

Allylation of Imines with *in situ* Generated Allyl Lead Reagents in a $PbBr_2/Al/BF_3 \cdot OEt_2/Et_2O$ System

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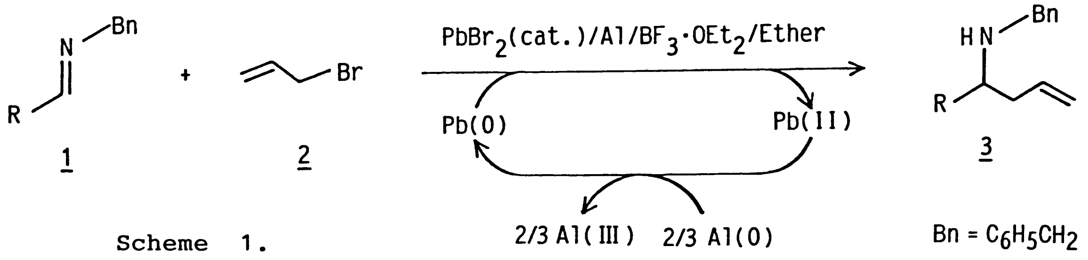
Reductive addition of allyl bromide to imines has been performed with a combination of a catalytic amount of $PbBr_2$ (0.03-0.1 equiv.) and Al (1 equiv.) in Et_2O containing $BF_3 \cdot OEt_2$ (1.1 equiv).

Among IVB group elements, Si and Sn have attracted much attention as powerful metals for various synthetic purposes, while Pb has been scarcely utilized except for the $Pb(OAc)_4$-oxidation.1) In a previous paper, we have reported "Barbier-type" allylation of carbonyl compounds with allyl halides in a $PbBr_2$/Al/DMF system, demonstrating that the *in situ* generated allyl lead reagent can be utilized for the synthetic purpose.2) In the course of the continuing studies, we now found that the *in situ* generated allyl lead reagent can effect the allylation of imines **1** in a slightly modified medium (Scheme 1).



Scheme 1.

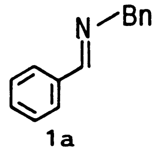
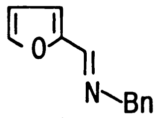
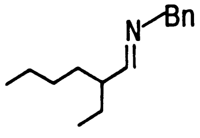
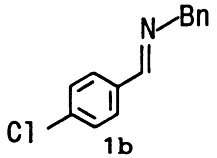
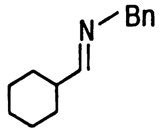
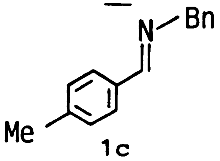
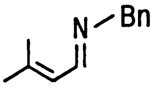
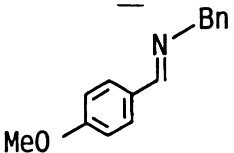
The present Pb-promoted allylation of imines **1** is characterized by the exceptionally simple operation compared with the hitherto disclosed allylation of imines **1** with various allyl metals; e.g., allyl boronates, allyl-9-BBN, allyl stannanes, allyl magnesium, and allyl zinc compounds.3) Thus, only mixing of imines **1** and allyl bromide **2** with a catalytic amount of $PbBr_2$ (0.03 equiv.) and aluminium foils (1 equiv.) in Et_2O containing $BF_3 \cdot OEt_2$ (1.1 equiv.)4) at ambient temperature affords the corresponding homoallylamines **3**.

Representative results are shown in Table 1. Allylation of aromatic and aliphatic aldimines **1a**-**1h** proceeds smoothly to afford the corresponding amines **3a**-**3h** in 50-94% yields (entry 1-9), while ketimines derived from acetophenone and cyclohexanone afford no appreciable allylation products. Notably, under similar conditions, benzaldehyde was recovered intact in contrast to the allylation in a $PbBr_2$/Al/DMF system.2)

Though details of the mechanism are not clear yet, it is likely that Pb metal generated on the aluminium foils plays a significant role in the formation of allyl lead reagents as well as the following reaction with imines <u>1</u> since Al alone or Pb(0) plate (99.9% pure) can not effect the allylation at all. Further applications of the unique combination of $PbBr_2/Al/BF_3$ OEt_2 are in progress.

The present work was partially supported by a Grant-in-Aid for Sientific Research No. 61225018 from the Ministry of Education, Science and Culture.

Table 1. Allylation of Imines in a $PbBr_2/Al/BF_3$ OEt_2/Et_2O System[a)]

Entry	1	2 (equiv.)	Time h	Yield[b)] %	Entry	1	2 (equiv.)	Time h	Yield[b)] %
1	 1a	1.5	10	84	6	 1e	1.5	8	78
2	1a	2	7	93[c)]	7	 1f	1.5	5	72
3	 1b	1.5	10	94	8	 1g	1.5	5	90
4	 1c	2	15	64[d)]	9	 1h	1.5	12	53[e)]
5	 1d	2	12	50[d)]					

a) Unless otherwise noted, reaction was carried out as described in the text. b) Isolated yield after column chromatography (SiO_2, hexane/AcOEt:5/1). c) With 0.1 equiv. of $PbBr_2$. d) With 2.0 equiv. of $BF_3 \cdot OEt_2$. e) 1,2-Adduct.

References

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4) $Al(O\text{-}Pr^i)_3$ and $Ti(O\text{-}Pr^i)_4$ can be used in place of BF_3 OEt_2 while in the absence of the Lewis acids, imines <u>1</u> were recovered.

(Received January 28, 1987)