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Metallic Bismuth and Tantalum Mediated C-Allylation of Aldimines with Allyl Bromide

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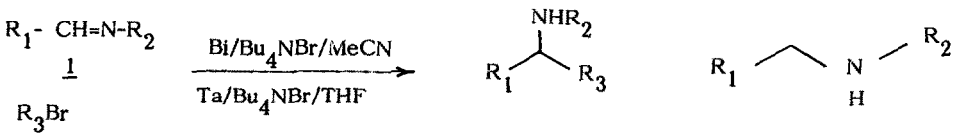
Abstract : A facile method for the synthesis of homoallyl amines using Bi/Bu_4NBr/MeCN and Ta/Bu_4NBr/THF system has been performed in a regiospecific manner.

There has been growing interest in the use of metals in organic synthesis and various metals have been successfully used for Barbier-type allylation of carbonyl compounds and aldimines to yield homoallyl alcohols and secondary amines respectively[1]. This communication describes the first example of bismuth and tantalum promoted allylation of aldimines 1 in a Bi/Bu_4NBr/MeCN and Ta/Bu_4NBr/THF system. The reaction proceeds smoothly under mild conditions to the hitherto disclosed allylation of imines with various allylmetals to afford homoallylamines in excellent yields[2].

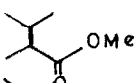
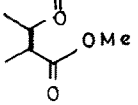
In a typical procedure (entry 1) to a solution of Bu_4NBr (709 mg, 2.2 mmol) in dry acetonitrile (10 ml) was added a mixture of allyl bromide (366 mg, 3 mmol) and benzylidine aniline 1a (398 mg, 2.2 mmol) followed by addition of bismuth powder. The reaction mixture was stirred at room temperature for 10 min. and then quenched with water. The product was extracted with dichloromethane (3 x 25 ml) and purified by column chromatography on silica gel to afford homoallyl amine 3a in 95% yield. Under identical conditions, Ta/Bu_4NBr/THF system gave lower yield (60%) of homoallyl amine 3a. Ketimines derived from acetophenone and cyclohexanone gave no allylated products. Chirality transfer has been demonstrated by reacting N-benzal-l-valine methyl ester with allyl bromide in Bi/Bu_4NBr/MeCN system which affords a 30:70 mixture of the adduct 3f and 3g in 85% yield.



The effect of Bu_4NBr is found to be remarkable and virtually no allylation occured in its absence. Me_3SiCl and NaI in place of Bu_4NBr was less effective and reduced imines were obtained in 60% and 30% yield respectively. When we attempted to homoallylate the carbonyl compounds with above reagents Bi/Bu_4NBr/MeCN system gave almost quantitative yields of the corresponding homoallylic alcohol with benzaldehyde and cyclohexanone while Ta/Bu_4NBr/MeCN system remained unreactive.

Tantalum and bismuth mediated synthetic reactions have been scarcely studied[3] and the present allylation of aldimines is remarkable with regard to its generality, less time, excellent yields and mildness of reaction conditions.

Table : Bismuth and Tantalum Mediated Allylation of Aldimines 1[a]

Compound	R_1	R_2	R_3	Time(mins) Bi/Bu_4NBr	Yield (%)[b]	Time(hrs) Ta/Bu_4NBr	Yield (%)
3a	Ph	Ph		10	95	10	60
3b	Ph	Me		10	85	12	46
3c	Ph 	CH_2Ph		9	92	10	46
3d	Ph 	Ph		8	95	10	55
3e		CH_2Ph		11	85	15	50
3f	Ph			12[4]	85	-	-
3g	Ph			12[4]	85	-	-

[a] The products were identified by comparison of mp/bp and spectral data with standard samples.
[b] Isolated yield after column chromatography.

References :

1. For some recent reports see: (a) Oda, Y.; Matsuo, S.; Saito, K. Tetrahedron Lett. 1992, 33, 97. (b) Li, C.J.; Chan, T.H. Tetrahedron Lett. 1991, 32, 7017. (c) Araki, S.; Katsumurs N.; Ito, H.; Butsugan, Y. Tetrahedron Lett. 1989, 30, 1581. (d) Beuchet, P.; Le, Marree, N.; Mosset, P. Tetrahedron Lett. 1992, 33, 5959. Agoston, G.E.; Cabal, M.P.; Turos, E. Tetrahedron Lett. 1991, 26, 3001. Yamamoto, Y. Acc. Chem. Res. 1987, 20, 243. Higashiyama, K.; Inoue, H.; Takahashi, H. Tetrahedron Lett. 1992, 33, 235 and references cited therein.

2. Keck, G.E.; Enholm, E.J. J. Org. Chem. 1985, 50, 146. Yamamoto, Y.; Nishii, S.; Maruyama, K.; Komatsu, T.; Ito, W. J. Am. Chem. Soc. 1986, 108, 7778. Kira, M.; Hino, T.; Sakurai, H. Chem. Lett. 1991, 277 and Bocoum, A.; Boga, C.; Savoia, D.; Umani, R.A. Tetrahedron Lett. 1991, 32, 1367 and references cited therein.

3. For the application of less explored bismuth see: Wada, M.; Takeichi, E.; Matsumoto, T. Bull. Chem. Soc. Jpn. 1991, 64, 990 and references cited therein. For scarcely studied tantalum see: Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. J. Org. Chem. 1992, 57, 1973.

4. The yields and diastereomeric ratios were determined by GC-MS analysis. The configuration of the two diastereoisomers has not been determined.

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