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Junquan Wang ^a , Jianqin Zhou ^a & Yongmin Zhang ^a ^a Department of Chemistry , Hangzhou University , Hangzhou, 310028, P. R. China Published online: 21 Aug 2006.

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FACILE PREPARATION OF HOMOALLYL AMINES VIA REACTION OF N-AMINOALKYLBENZOTRIAZOLES WITH ALLYLSAMARIUM BROMIDE

Junquan Wang, Jianqin Zhou and Yongmin Zhang

Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China

ABSTRACT: Homoallyl amines can be readily prepared in good to excellent yields via reaction of N-aminoalkylbenzotriazoles with allylsamarium bromide in THF at room temperature.

Homoallyl amines are useful precursors of a variety of compounds by functionalization of the double bond^[1]. An important strategy for the preparation of homoallyl amines rests on the addition of allylmetallic species to the carbon-nitrogen double bond in imines^[2], but it is not suitable for the preparation of homoallyl tertiary amines.

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[.] To whom correspondence should be addressed.

In recent years, much attention has been paid to the application of samarium reagents to organic synthesis, especially $\text{SmI}_2^{[3]}$, which can promote the Barbier-type reaction between carbonyl compounds and alkyl halides. Recently, S. H. Wu et al reported the Barbier-type allylation of ketones^[4] and carboxyllic esters^[5] with samarium and allyl bromide. An organosamarium intermediate reaction mechanism has been suggested. We have also reported the allylation of imines with allylsamarium bromide^[6].

N-Aminoalkylbenzotriazoles 1 have been shown to exist in solution in equilibrium with iminium ions (Scheme) and this characteristic has led to the development of a number of useful synthetic applications based on their reaction with nucleophiles with the expulsion of the benzotriazoles moiety^[7]. In this paper, we wish to report a novel preparation of homoallyl amines 2 via reaction of Naminoalkylbenzotriazoles with allylsamarium bromide. In our experimental work, it was found that N-aminoalkylbenzotriazoles reacted smoothly with allylsamarium bromide to afford homoallyl amines in good to excellent yields at room temperature (Scheme). Some results were summarized in Table.

Scheme

Bt Bt⁻ CH₂CH = CH₂

$$R^{1}$$
-CH-NR²R³ R¹-CH=N⁺R²R³ CH₂=CHCH₂SmBr R¹-CH-NR²R³
1 2

Bt ; Benzotriazol-1-yl (a) ; $R^1 = H$, $R^2 = H$, $R^3 = C_6 H_5$; (b) ; $R^1 = H$, $R^2 = H$, $R^3 = 3$ -ClC₆H₄;

(c):
$$R^{1} = H$$
, $R^{2} = H$, $R^{3} = 3$ -CH₃C₆H₄;
(d); $R^{1} = H$, $R^{2} = H$, $R^{3} = 4$ -CH₃C₆H₄;
(e): $R^{1} = H$, $R^{2} = CH_{3}$, $R^{3} = C_{6}H_{5}$;
(f): $R^{1} = H$, $R^{2} = H$, $R^{3} = C_{6}H_{5}CH_{2}$;
(g): $R^{1} = C_{6}H_{5}$, $R^{2} = H$, $R^{3} = C_{6}H_{5}$;
(h): $R^{1} = C_{6}H_{5}$, $R^{2} = H$, $R^{3} = 4$ -ClC₆H₄;

Table . Preparation of homoallyl amines.

Product	Yield * (%)	^I H-NMR(CCl ₄),δ(ppm)
2a	90	2. $17-2.51(q, 2H), 2.90-3.20(t, 2H), 4.$ 77-6. $0(m, 3H), 6.24-7.24(m, 5H)$
2b	89	2. 20-2. 60(q,2H), 3. 0-3. 33(t,2H), 4. 80 -6. 0(m,3H), 6. 20-7. 16(m,4H)
2c	93	2. $0(s, 3H)$, 2. $23-2$. $63(q, 2H)$, 3. $03-3$. 36 (t, 2H), 4. $83-6$. $06(m, 3H)$, 6. $33-7$. 16 (m, 4H)
2d	91	1. 96-2. 47(m,5H),2. 90-3. 20(t,2H),4. 73-5. 96(m,3H),6. 17-7. 0(m,4H)
2e	87	2. $0-2$. $50(q, 2H)$, 2. $84(s, 3H)$, 3. $14-3$. 53 (m, 2H), 4. $53-6$. $0(m, 3H)$, 6. $33-7$. 16 (m, 5H)
2f	88	2. $11-2.45(q, 2H), 2.87-3.17(t, 2H), 3.$ 84(s, 2H), 4.74-6.0(m, 3H), 7.30(s, 5H)
2g	76	2. $15-2.64(t, 2H)$, 3. $95-4.32(t, 1H)$, 4. $59-5.72(m, 3H)$, 5. $95-7.23(m, 10H)$
2h	72	2. $18-2.56(t, 2H), 4.13-4.46(t, 1H), 4.$ 74-5.75(m, 3H), 5.91-7.24(m, 9H)

* Yields of isolated products.

* * All products gave satisfactory IR spectra.

Experimental

The solvent tetrahydrofuran was freshly distilled from sodium/ benzophenone ketyl before its use. ¹H-NMR spectra were recorded on a JEOL JOM-PMX 60SI(60MHZ) instrument using TMS as internal standard. IR spectra were recorded with a PE-683 spectrometer. All substrates were easily prepared from corresponding aldehydes, amines and benzotriazole^[7].

General procedure for the preparation of homoallyl amines:

Under inert atmosphere of nitrogen, powdered samarium (0. 15g, 1mmol) was placed in a 50ml three-neck flask and a solution of allylbromide (0. 15g, 1. 25mmol) in 10 ml THF was added by syringe. The mixture was magnetically stirred for 1 h at room temperature. A purple suspension was obtained. Then N-aminoalkylbenzotriazole(1mmol) was added to this suspension in one portion under inert atmosphere of nitrogen. The mixture was stirred for 0. 5-1 hr at room temperature. A dilute solution of $K_2CO_3(5\%, 5ml)$ and ether(20ml) were added. The organic layer was seperated and the aqueous layer was extracted with ether($10ml \times 2$). The combined organic solution was washed with water ($20ml \times 2$) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel(cyclohexane/acetate as eluent).

In view of the easily available starting materials, good yield, simple operation, mild and neutral reaction conditions, the present procedure provides a useful method for the preparation of homoallyl amines. Acknowledgement: We are grateful to the National Natural Science Foundation of China for financial support.

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