Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

The Synthesis of Homoallylamines by the Addition of Organosamarium Reagent to Nitriles

Mingxin Yu [a] , Yongmin Zhang [a] & Hongyun Guo [a]
[a] Department of Chemistry, Hangzhou University, Hangzhou, 310028, P. R. China

Available online: 22 Aug 2006

To cite this article: Mingxin Yu, Yongmin Zhang & Hongyun Guo (1997): The Synthesis of Homoallylamines by the Addition of Organosamarium Reagent to Nitriles, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:9, 1495-1500

To link to this article: http://dx.doi.org/10.1080/00397919708006085

SYNTHETIC COMMUNICATIONS, 27(9), 1495-1500 (1997)

THE SYNTHESIS OF HOMOALLYLAMINES BY THE ADDITION OF ORGANOSAMARIUM REAGENT TO NITRILES

Mingxin Yu, Yongmin Zhang*, Hongyun Guo
Department of Chemistry, Hangzhou
University, Hangzhou, 310028, P. R. China

Abstract: Organosamarium reagent reacts with nitriles to afford homoallylamines in THF.

The application of samarium diiodide in organic synthesis has received more and more attention in the last decade[1]. However, studies on application of samarium metal in organic synthesis were very few[2]. Curran firstly reported the samarium Grignard reaction[3]. Our group have studied the reaction of organosamarium reagent with imine and the synthesis of allyl selenides by organosamarium reagent[4]. The addition of allylic organometallics to nitriles is

* To whom correspondence should be addressed.

an important synthetic method for the preparation of homoallylic amines, Earlier methods mostly suffer from low yields[5]. It has been constantly improved over the years by changing the allylmetallics from magnesium over lithium, zinc, aluminum to boron and tin[6]. Yasuo Butsugan reported on reaction of allylation of nitriles with allylindate[7]. Their method was that solution of allylindium sesquibromide, prepared from indium powder and allyl bromide in dioxane at room temperature for 40 min, was added methyllithium at 0℃ and was stirred at room temperature for 2h, then was added benzonitrile, and the whole mixture was stirred at room temperature for 2h to give homoallylic amines. Herein we wish to report that the reaction of organosamarium reagent with nitriles, which affords homoallylic amines in good yield. The advantages of this method are rapid reaction, simple operation, mild and neutral condition. The results were summarized in table 1.

$$CH_2{=}CH{-}CH_2Br + Sm \xrightarrow[r.t.]{THF} CH_2{=}CH{-}CH_2SmBr$$

$$R{-}C{\equiv}N + 2CH_2{=}CH{-}CH_2SmBr \xrightarrow[r.t.,2h]{THF} R{-}C(CH_2{-}CH{=}CH_2)_2{-}NH_2$$

R: C_6H_5, m−$CH_3C_6H_4$, p−$CH_3C_6H_4$, $C_6H_5CH_2$,

$CH_2{=}CH$, $C_6H_5S(=O)_2CH_2$, p−$CH_3C_6H_4S(=O)_2CH_2$

Experimental Section

Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately before use. Elemental analyses were carried out using a Carlo Erba 1106

Table 1. Reaction Condition and yield of Products

NO.	Products	Reaction Condition		yield*
		Time(h)	temperature	(%)
1	$C_6H_5C(C_3H_5)_2NH_2$	2	r.t.	78
2	$m-CH_3C_6H_4C(C_3H_5)_2NH_2$	2	r.t.	81
3	$p-CH_3C_6H_4C(C_3H_5)_2NH_2$	2	r.t.	74
4	$C_6H_5CH_2C(C_3H_5)_2NH_2$	2	r.t.	69
5	$CH_2CHC(C_3H_5)_2NH_2$	2	r.t.	66
6	$C_6H_5\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_2C(C_3H_5)_2NH_2$	2	r.t.	77
7	$p-\ CH_3C_6H_4\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_2C(C_3H_5)_2NH_2$	2	r.t.	71

* Yield of isolated product

instrument, IR spectra were recorded on a PE—683 spectrometer, ^1H NMR spectra were obtained with a PMX—60 spectrometer in $CDCl_3$ solution using TMS as internal standard.

General procedure for the synthesis of homoallylamines, 0.33g (2.2mmol) samarium and 20ml THF, 0.30g(2.5mmol) allyl bromide were added to a three necked flask with stirring at room temperature under nitrogen. When the mixture became purple, continue to stir for 1h until the samarium powder disappar. Nitriles were then added to the solution, and the mixture was stirred at room temperature under nitrogen for 2h, 10ml water was added. The reaction mixture was extracted with ether (40ml×3) and the

ether layer was seperated. The ethereal solution was washed with water (40ml $\times 3$), dried over $MgSO_4$, The solvent was removed by evaportation under reduced pressure. The crude product was purified by preparative TLC on sillica gel (dicholomethane as eluent). The products were identified by elemental analyses, IR and ^1H NMR spectra.

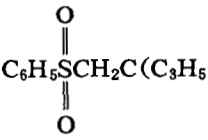
$C_6H_5C(C_3H_5)_2NH_2$, oil,[7] IR (film), 3380, 3075, 3015, 2985, 1640, 1500, 1445, 760, 705, cm^{-1}, ^1H NMR, 7.50—6.93(m, 5H), 5.78—5.40(m, 2H), 5.23—4.70(m, 4H), 2.70—2.34(m, 4H), 1.96—1.75(s, 2H), ppm.

$m-CH_3C_6H_4C(C_3H_5)_2NH_2$, oil, IR (film), 3400, 3100, 3000, 2945, 1695, 1652, 1620, 1450, 920, 785, 708, cm^{-1}, ^1H NMR, 7.36—6.80(m, 4H), 5.80—5.36(m, 2H), 5.20—4.70(m, 4H), 2.63—2.20(m, 7H), 2.10—1.83 (S, 2H), ppm. Anal. Calcd. for $C_{14}H_{19}N$: C, 83.53; H, 9.513; N, 6.958; Found: C, 83.31; H, 9.515; N, 6.936.

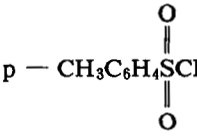
$p-CH_3C_6H_4C(C_3H_5)_2NH_2$, oil, IR (film), 3405, 3080, 2960, 2870, 1640, 1510, 990, 915, 830, 710, cm^{-1}. ^1H NMR, 7.40—6.81(m, 4H), 5.83—5.34 (m, 2H), 5.23—4.71(m, 4H), 2.68—2.18(m, 7H), 2.10—1.85(s, 2H), ppm. Anal. Calcd. for $C_{14}H_{19}N$: C, 83.53; H, 9.513; N, 6.958; Found: 83.40; H, 9.498; N, 6.949.

$C_6H_5CH_2C(C_3H_5)_2NH_2$, oil[5], IR (film), 3390, 3090, 2960, 2880, 1643, 1505, 1462, 918, 752, 700, cm^{-1}, ^1H NMR, 7.20—6.87(m, 5H), 5.90—5.43 (m, 2H), 5.20—4.77(m, 4H), 2.70—2.40(m, 2H), 2.34—1.98(m, 4H), 1.89—1.70(s, 2H), ppm.

$CH_2CHC(C_3H_5)_2NH_2$, oil, IR (film), 3020, 2960, 2935, 1645, 1385, 1165, 990, 910, cm^{-1}, ^1H NMR, 5.90—5.30(m, 3H), 5.23—4.63(m, 6H), 2.67—2.34(m, 4H), 2.07—1.78(s, 2H), ppm. Aanl. Calcd. for $C_9H_{15}N$: C, 78.78; H, 11.02; N, 10.21; Found: C, 78.54; H, 10.93; N, 10.12.



, oil, IR (film), 3400, 3095, 2970, 2890, 1650, 1500, 1465, 920, 740, cm^{-1}, ^1H NMR, 7.93—7.30(m, 5H), 5.93—5.40(m, 2H), 5.30—4.70(m, 4H), 4.10—3.93(s, 2H), 2.40—2.14(m, 4H), 2.08—1.85(s, 2H), ppm. Anal. Calcd. for $C_{14}H_{19}NO_2S$: C, 63.37; H, 7.216; N, 5.278; Found: C, 63.18; H, 7.221; N, 5.271.



, oil, IR (film), 3398, 3093, 2965, 1648, 1489, 1180, 990, 915, 742, cm^{-1}, ^1H NMR, 7.89—7.32(m, 4H), 5.90—5.39(m, 2H), 5.29—4.73(m, 4H), 4.08—3.90(s, 2H), 2.59—2.18(m, 7H), 2.10—1.81(s, 2H), ppm. Anal. Calcd. for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.576; N, 5.013; Found: C, 64.26; H, 7.568; N, 5.047.

Acknowledgement

We thank the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial support.

References

1. a) Girard, P., Namy, J. L., Kagan, H. B., *J. Am. Chem. Soc.*, **1980**, *102*, 2693

   b) Molender, G. A., *Chem. Rev.*, **1992**, *92*, 29

   c) Molender, G. A., Harris, C. R., *Chem. Rev.*, **1996**, *96*, 307

2. FuKuzawa, S., Fujinami, S., *J. Chem. Soc. Chem. Commun.*, **1986**, 475.

3. Curran, D. P. , Totleben, M. J. , *J. Am. Chem. Soc.* ,**1992**, *114*, 6050

4. a) Wang J. Q. , Zhang Y. M. , *Synth. Commun.* ,in Press.

b) Yu M. X. , Zhang Y. M. , Bao W. L. , *Synth. Commun.* , in Press.

5. Benkeser, R. A. , *Synthesis*, **1971**, 347

6. a) Keck, G. E. , Enholm, E. J. , *J. Org. Chem.* , **1985**, *50*, 146

b) Yamamoto, Y. , Komatsu T. , and Maruyama K. , *J. Org. Chem.* , **1985**, *50*, 3115.

c) Wuts, P. G. M. , Jung, Y. W. , *Tetrahedron Lett.* ,**1986**, *27*, 2079

d) Ciganek E. , *J. Org. Chem.* , **1992**, *57*, 4521.

7. Shun Ji Jin, Shuki Araki, and Yasuo Butsugan, *Bull. Chem. Soc. Jpn.* , **1993**, *66*, 1528

(Received in the UK 10 October 1996)