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Facile Reduction of Azides to the Corresponding Amines with Metallic Samarium and Catalytic Amount of Iodine

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Abstract: Samarium and a catalytic amount of iodine in methanol reduce alkyl and aryl azides to the corresponding amines, and aroyl, sulfonyl azides to the corresponding amides in good yields under neutral and mild condition.
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Since azides can be prepared with good regio—, stereo— and enantio control[1-3] and subsequent reduction permits controlled introduction of amino function. The reduction of azides to amines is an important reaction in organic synthesis, A wide variety of reagents including zinc borohydride[4], borohydride exchange resin (BER)-nickel acetate[5], Lithium aminoborohydrides[6], Sodium borohydride /copper (II) sulphate[7]. benzyltriethylaminonium tetrathiomolybdate[8], etc. for this purpose have been reported recently.

Samarium diiodide as a powerful one-electron transfer reductant has been widely used in organic synthesis in the last decade[9]. However, there are some problems when it is used as a reductant, for example, it is expensive and needs delicate treatment and careful storage because it is very sensitive to air oxidation. It is known that SmI_2 can be prepared from equimolar samarium and iodine in THF by refluxing overnight[10]. Metallic samarium has a stronger reducing power ($Sm^{3+}/Sm = -2.41V$) than that of SmI_2 ($Sm^{3+}/Sm^{2+} = -1.55V$) and it has been noted recently that cheap and stable metallic samarium can be used directly as a reductant instead of SmI_2 in organic synthesis[11]. It has been known that azides could be reduced with SmI_2 to the corresponding amines[12], but there is no report on such a reaction by the direct use of samarium. Here we wish to report reduction of azides to the corresponding amines or amides with samarium and catalytic amount of iodine in high yield in methanol under mild and neutral condition.

Table 1 summarizes our results on the reduction of a number of alkyl, aryl, aroyl and arylsulfonyl azides. In all the reactions, the cleavage takes place between the N—N bond, rather than the C—N or S—N bond. At the same time, aryl, aroyl and arylsulfonyl azides containing halides, carbonyl, or sulfonyl groups are reduced to the corresponding amines or amides. The amides are not reduced further to the amines. Chloro, bromo, iodo, carbonyl and sulfonyl groups cannot be reduced under the reaction conditions and do not influence the rate of reduction. Therefore, a novel method for the preparation of amines from azides has been developed and the high yields of the reduction products demonstrate the efficiency of this new method.

In conclusion, with high yields, mild and neutral conditions as well as straightforward procedure, we think that the present work described herein may not only provide a useful method for the conversion of azides to amines, but also open a new way for using metallic samarium directly in organic synthesis.

Table Ⅰ. Reduction of azides to amines by Sm and catalytic amount of iodine

Entry	Azides[a]	Conditions	Yield %[b,c]	Entry	Azides[a]	Conditions	Yield %[b,c]
1	$4-ClC_6H_4N_3$	r.t. 6 h	86	9	$n-C_7H_{15}N_3$	r.t. 6h reflux 2h	76
2	$4-BrC_6H_4N_3$	r.t. 6 h	93	10	$n-C_8H_{17}N_3$	r.t. 6h reflux 2h	79
3	$4-IC_6H_4N_3$	r.t. 6 h	91	11	$C_6H_5CON_3$	r.t. 6h reflux 2h	88
4	$4-CH_3C_6H_4N_3$	r.t. 6 h	84	12	$3-CH_3C_6H_4CON_3$	r.t. 6h reflux 2h	83
5	$2-CH_3C_6H_4N_3$	r.t. 6 h	84	13	$C_6H_5SO_2N_3$	r.t. 6h reflux 2h	89
6	$2.4-Cl_2C_6H_3N_3$	r.t. 6 h	86	14	$4-CH_3C_6H_4SO_2N_3$	r.t. 6h reflux 2h	93
7	$C_6H_5N_3$	r.t. 6 h	87	15	$N_3CH_2COOC_2H_5$	r.t. 6h	74[e]
8	$2\text{-}HOOCC_6H_4N_3$	r.t. 6h	70[d]				

a. all azides were prepared according to ref. 5 and 13 b. isolated yield. c. all products are known compounds and gave satisfactory m.p., IR and ^{1}HNMR spectra. d. product was $2\text{-}H_2NC_6H_4COOCH_3$ e. product was $H_2NCH_2COOCH_3$

A typical procedure is as follows: 0.15g(1 mmol) of Sm and 0.05g(0.2 mmol) of iodine were mixed in a three neck round bottom flask under nitrogen. 1 mmol of azide in 5ml of methanol was added by syringe to the mixture which was stirred at room temperature and the reaction monitored by TLC. After the reaction was complete, the reaction mixture was diluted with 50 ml of ether and filtered, the filtrate was washed with satd. aq. $Na_2S_2O_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude product purified by preparative TLC.

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REFERENCES

1. Hodgson, H. H. and Norris W. H. H, *J. Chem. Soc.*, **1949**, 762—763
2. Ito, M.; Koyakumaru, K. and Takaya, T. H., *Synthesis*, **1995**, 376—378
3. Seriven, E. F. V., Turnbull, K., *Chem. Rev.*, **1988**, 88, 297
4. Ranu, B. C.; Sarkar, A. and Chakraborty, R., *J. Org. Chem.*, **1994**, 59, 4114—4116
5. Yoom, N. M.; Choi, J. and Shon, Y. S., *Synth. Commun.*, **1993**, 23, 3047—3053
6. Alvarez, S. G.; Fisher, G. B. and Singavam, B., *Tetrahedron Lett.*, **1995**, 36, 2567—2570
7. Rao, H. S. P. and Siva, P. *Synth. Commun.*, **1994**, 24, 549—555
8. Ramesha, A. R.; Bhat, S. and Chandrasekan, S., *J. Org. Chem.*, **1995**, 60, 7682
9. Molander, G. A., *Chem. Rev.*, **1992**, 92, 29—68
10. Imamoto, T. and Ono, M.; *Chem. Lett.*, **1987**, 501
11. Ogawa, A.; Nanke, T.; Takam, N.; Sumino, Y.; Ryu, I. and Sonoda, N., *Chem. Lett.*, **1994**, 379
12. Dubois, C. G. and Hesse, M., *Tetrahedron Lett.*, **1995**, 36, 7427—7430
13. Reeves, W. P.; Bahr, M. L., *Synthesis*, **1976**, 823

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