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REDUCTION OF AZIDES TO AMINES WITH SmI_2 OR Cp_2TiCl_2-Sm SYSTEM

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ABSTRACT: Azides can be rapidly reduced to corresponding amines with SmI_2(Method A) or Cp_2TiCl_2-Sm system(Method B) in good yields under mild conditions.

Since azides can be easily prepared with good regio-and stereocontrol and subsequent reduction permits controlled introduction of amino function, the conversion of azides to corresponding amines is an important reaction in organic synthesis. As a result, many reagents, especially borohydride series reductants[1,2,3], have been used for the reduction of azides to amines. Recently, A. Capperucci[4]et al. have also reported a new method.

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Over the last decade, there has been growing interest in the use of samarium reagents, in particularly SmI_2[5], in organic synthesis. We have previously reported the reduction of some organic compounds by SmI_2[6,7,8,9] or Cp_2TiCl_2-Sm system[10]. Herein we wish to report two novel methods for the reduction of azides to amines with SmI_2 (Method A) or Cp_2TiCl_2-Sm system (Method B). In our experimental work, we have found that aryl, alkyl and aroyl azides can be repidly reduced to corresponding amines in good yields in THF at room temperature with SmI_2 or Cp_2TiCl_2-Sm system (Scheme). In these reactions, the reductive cleavage of N-N bond other than C-N bond took place. Some results were summurized in Table 1. From the results, we think that Cp_2TiCl_2-Sm system is more efficient than SmI_2 for the reduction of azides to amines. The further synthetic utilization of the former is under investigation.

Scheme

$$\underset{1}{R-N_3} \xrightarrow[\text{Method B. } Cp_2TiCl_2\text{-Sm/t BuOH, r. t.}]{\text{Method A. } SmI_2\text{/t-BuOH, r. t.}} \underset{2}{R-NH_2}$$

(a): $R=4\text{-}ClC_6H_4$ (b) $R=4\text{-}BrC_6H_4$;

(c): $R=4\text{-}CH_3C_6H_4$ (d) $R=2\text{-}CH_3C_6H_4$;

(e): $R=2,4\text{-}Cl_2C_6H_3$ (f) $R=C_6H_5$;

(g): $R=C_6H_5CO$ (h) $R=3\text{-}CH_3C_6H_4CO$;

(i): $R=C_7H_{15}$ (j) $R=C_8H_{17}$;

Experimental

Tetrahydrofuran was freshly distilled from sodium/ benzophenone ketyl and t-butanol was distilled from anhydrous

Table 1. Reduction of azides to amines with Method A or Method B.

Product	Reaction time(min.)		Yield* (%)	
	Method A	Method B	Method A	Method B
2a	20	5	71	78
2b	26	5	76	81
2c	30	5	65	75
2d	60	5	61	84
2e	15	5	80	74
2f	20	5	75	86
2g	10	5	83	87
2h	20	5	81	80
2i	30	5	70	76
2j	30	5	73	79

* Yields of isolated products.

* * All products are known compounds and gave satisfactory m. p. , IR and ^{1}H-NMR spectra.

$MgSO_4$ before their use. All azides were prepared according to known method[11]. IR spectra were determined on a PE-683 spectrometer. ^{1}H-NMR spectra were recorded by a PMX-60MHZ spectrometer using TMS as internal standard.

General procedure for the reduction of azides by SmI_2 or Cp_2TiCl_2-Sm system:

Method A: Under an inert atmosphere of nitrogen, to a magnetically stirred solution of SmI_2(4mmol) prepared in situ from 0. 6g samarium powder and 1g iodine in 30ml THF, azide (1mmol) and t-butanol(2mmol) in 2ml THF was added in one portion. The deep blue colour of SmI_2 solution disappeared within 1 minute and turned to brown. After stirring for some time (described in Table), the solvent was removed under reduced pressure. The residue was diluted with 20ml satd. aq. $Na_2S_2O_3$ and then extracted by ether

(20ml×3). The organic layer was washed with satd. aq. $Na_2S_2O_3$ (20ml×3) and brine(20ml×3) and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by preparative TLC on siliga gel(dichloromethane: cyclohexane=3 : 2 as eluent).

Method B: Under an inert atmosphere, 0. 20g (1. 33mmol) samarium powder, 0. 67g (2. 67mmol) Cp_2TiCl_2 and 15ml THF were added to a 50ml three-neck flask. The mixture was magnetically stirred for 0. 5hr at refluxing temperature and then cooled to room temperature. A blue solution was obtained. Azide (1mmol) and 0. 15g (2mmol) t-butanol in 2ml THF was then added to this stirred blue solution, the blue solution turned red at once. After 5 minutes, TLC monitoring of reaction indicated that the corresponding amine had been produced and that the substrate had been cousumed entirely. The subsequeut opreration was the same as Method A.

In view of good yield, simple operation, rapidity as well as mild and netruel conditions, we think that the present procedures provide two useful methods for the reduction of azides to amines.

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