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Reductive Coupling of Aldimines Mediated with Samarium Catalyzed by Cp_2TiCl_2

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REDUCTIVE COUPLING OF ALDIMINES MEDIATED WITH SAMARIUM CATALYZED BY Cp_2TiCl_2

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ABSTRACT: Reductive coupling of aldimines into vicinal diamines mediated with samarium catalyzed by Cp_2TiCl_2 proceeds in refluxing THF with good yields.

Despite the frequent occurrence of vicinal diamine units in natural products and medicinal agents[1], only a few methods are available for the preparation of vicinal diamines[2].Apparently, the reductive coupling of imines is a straightforward route to vicinal diamines. Recently, a few reagents have been employed for the formation of vicinal diamines, namely aluminium[3a], ytterbium[3b], indium[3c], titanium[3d], and SmI_2[3e]. These reports encouraged us to explore the reactions with our recently reported Cp_2TiCl_2/Sm system, which is a good reagent of reduction and coupling[4].

Accidentally, we found that the coupling reaction of aldimines could be carried out in refluxing THF with metallic samarium(1mmol) and a catalytic amount of Cp_2TiCl_2(0.1-0.2mmol)(Scheme 1). The reaction times and product yields are listed in Table 1.

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Scheme 1

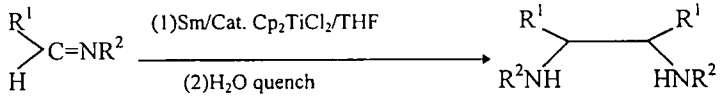


Table 1: Reductive Coupling of Aldimines to Vicinal Diamines[a]

product	R^1	R^2	Ratio of moles[b]	Reaction[c] Time(h)	Yield(%)[d] (dl:meso)[e]
1[9]	C_6H_5	C_6H_5	2:1:0.1	4	88(70:30)
2[10]	p-ClC_6H_4	C_6H_5	2:1:0.2	5	80(75:25)
3[10]	p-$CH_3C_6H_4$	C_6H_5	2:1:0.2	5	84(80:20)
4[3e]	C_6H_5	$C_6H_5CH_2$	2:1:0.2	6	75(85:15)
5[10]	p-$CH_3OC_6H_4$	C_6H_5	2:1:0.1	4	82(80:20)
6[11]	C_6H_5	p-BrC_6H_4	1:1:0.2	6	73(90:10)
7[8]	p-$(CH_3)_2NC_6H_4$	C_6H_5	1:1:0.2	9	67(80:20)
8[12]	C_6H_5	n-C_4H_9	1:1:0.2	9	57(60:40)
9[3e]	C_6H_5	c-C_6H_{11}	1:1:0.2	9	55(85:15)

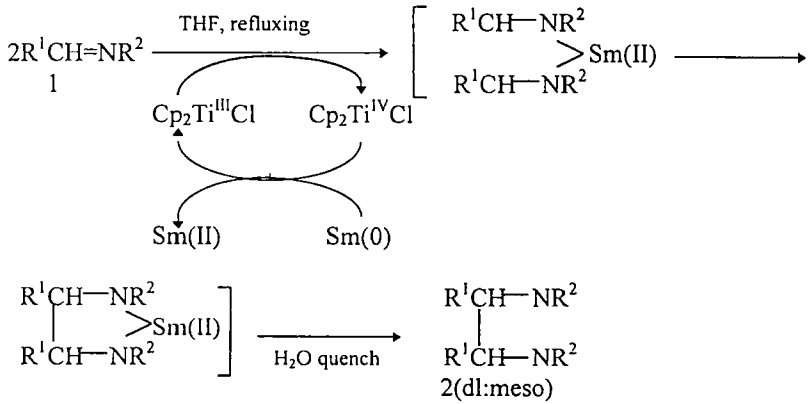
a. Carried out in the manner as described in the text unless otherwise noted; b. Ratio of moles of aldimine:samarium:Cp_2TiCl_2 ; c. The reaction time was monitored by TLC until most of imines was consumed; d. Isolated yields, the products were confirmed with IR and ^{1}H NMR;
e. Ratio of dl:meso is calculated from ^{1}H NMR.

The coupling reaction of aldimines can not be carried out without Cp_2TiCl_2 under the same conditions. Moreover, we have investigated the Cp_2TiCl_2/Sm system and obtained evidence of $Cp_2Ti^{III}Cl$ in the system[5]. Meanwhile, we have observed that $Cp_2Ti^{III}Cl$ which is prepared according to lit.[6] also mediated the reducting and coupling of aldimines. According to above experiment and referring to Kham[8], a possible mechanism is proposed (Scheme 2).

Experimental:

Starting materials - The aldimines were prepared from the freshly distilled

Scheme 2



aldehyde and aniline according to a published procedure[7]. Tetrahydrofuran was preparative TLC on silica gel (hexane:Et_2O=10:1)

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5.Prepration of Cp_2TiCl by reduction of Cp_2TiCi_2 with Sm. 0.15g(2mmol)Sm and 0.5g (2mmol) Cp_2TiCl_2 were mixed in a Schlenk type apparatus under a nitrogen atmosphere, then 10ml THF was added by syringe.After refluxing 0.5 h, a deep blue solution was obtained. The solvent was evaporated under reducing pressure. Benzene(5ml) was added and this benzene solution was preserved under a nitrogen atmosphere in the Schlenk flask, then a deep blue solid was gradually precipitated out. Recrystallization from hot benzene, gave deep blue crystals. Mass spectrum was recorded on a HP 5989A type apparatus. MS m/z(rel. intensity) 213(M^+,100), 178(96), 148(62), 83(10), 65(7).

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