



Reductive coupling of aliphatic cyclic imides with benzophenones by low-valent titanium



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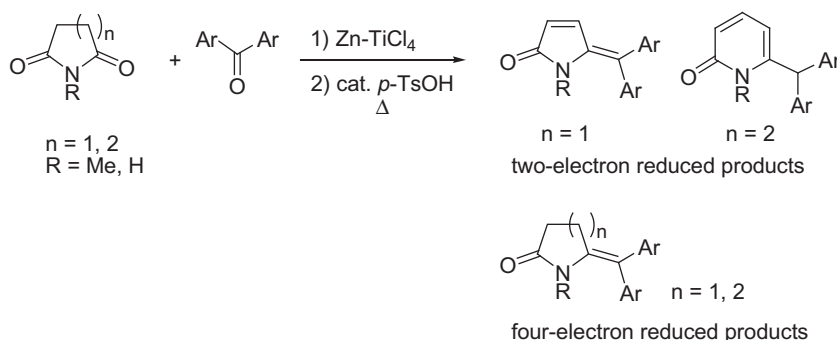
ABSTRACT

The reductive coupling of aliphatic cyclic imides with benzophenones by Zn–TiCl₄ in THF gave two- and four-electron reduced products selectively by controlling the reaction conditions. Although cyclic and acyclic products were formed as mixtures in most cases, cyclic dehydrated products could be selectively obtained by heating the product mixtures in the presence of cat. *p*-TsOH.

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Cross McMurry coupling is a powerful tool for the reductive coupling of two different carbonyl compounds because of its versatility, convenience, and economical efficiency.^{1,2} Recently, we reported the reductive coupling of uracils^{3a} and *N*-methoxycarbonyl lactams^{3b} with benzophenones by low-valent titanium. In this context, we report herein the reductive coupling of aliphatic cyclic imides, such as succinimides and glutarimides, with benzophenones by low-valent titanium generated from Zn–TiCl₄ (Scheme 1). We found that two- and four-electron reduced adducts could be selectively obtained by controlling the reaction condi-

tions. In each case, cyclic and acyclic products were formed depending on the substrates and the conditions of workup after the reductive coupling. In most cases, the products converged on cyclic dehydrated products by reflux of the product mixtures in benzene or toluene in the presence of cat. *p*-TsOH. Therefore, this method provides a synthetic route to a new class of five- and six-membered nitrogen heterocycles, 5-(diarylmethylene)-1*H*-pyrrol-2(5*H*)-ones, 6-diarylmethylpyridin-2(1*H*)-ones, and their hydrogenated analogs.⁴ The reaction mechanisms of the reductive coupling and following reactions are also discussed.

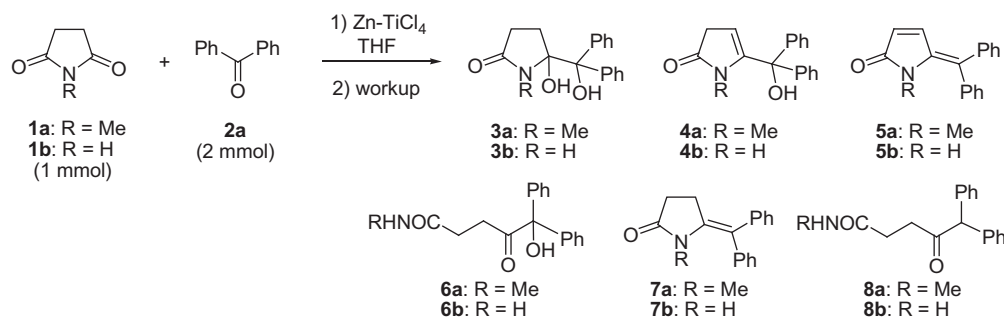


Scheme 1. Reductive coupling of aliphatic imides with benzophenones by Zn–TiCl₄.

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Table 1
Reductive coupling of **1a,b** with **2a** by Zn–TiCl₄



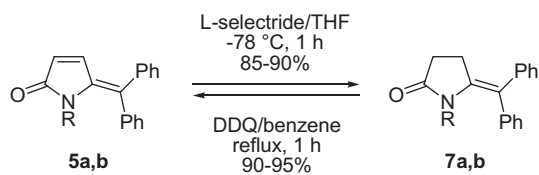
Run	1	TiCl ₄ ^a (mmol)	Temp (°C)	Workup ^b	Yield ^c (%)						
					3	4	5	6	7	8	
1	1a	2	0	a	a	18	13	20	32	—	—
2	1a	2	0	a ^d	a	—	—	73	10	—	—
3	1a	2	0	b	a	—	—	80	—	—	—
4	1a	2	0	c	a	18	—	—	61	—	—
5	1a	4	30	a	a	—	—	14	—	31	28
6	1a	4	30	b	a	—	—	12	—	54	—
7	1b	2	0	a	b	10	9	7	30	—	—
8	1b	2	0	b	b	—	—	53	—	—	—
9	1b	2	0	c	b	5	10	—	42	—	—
10	1b	4	30	a	b	—	—	7	—	36	13
11	1b	4	30	b	b	—	—	5	—	47	—

^a Zn/TiCl₄ = 2/1.

^b (a) 1 M HCl, 25 °C, 15 min; (b) crude product mixture obtained by workup with 1 M HCl (workup a) was refluxed in benzene in the presence of cat. *p*-TsOH for 30 min; (c) satd NaHCO₃ aq, 25 °C, 3 h.

^c Isolated yields.

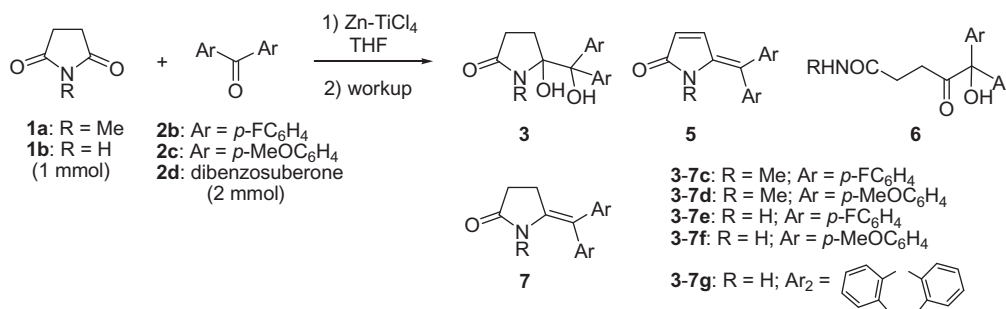
^d 1 M HCl, 25 °C, 3 h.



Scheme 2. Mutual transformation between **5a,b** and **7a,b**.

The reaction conditions of the reductive coupling were surveyed with *N*-methylsuccinimide (**1a**) and benzophenone (**2a**) as the substrates and the results are summarized in Table 1.⁵ The molar ratio of Zn/TiCl₄ was fixed to 2/1. First, the reduction was carried out with the ratio of **1a/2a**/TiCl₄ as 1/2/2 in THF at 0 °C for 12 h (runs 1–4). After usual workup with 1 M HCl at 25 °C for 15 min, four cross-coupled products **3a–6a** were formed as two-electron reduced products (run 1). When the workup time

Table 2
Reductive coupling of **1a,b** with **2b,c,d** by Zn–TiCl₄



Run	1	2	TiCl ₄ ^a (mmol)	Temp (°C)	Workup ^b	Yield ^c (%)				
						3	5	6	7	
1	1a	2b	2	0	b	c	—	81	—	—
2	1a	2b	2	0	c	c	—	—	71	—
3	1a	2b	4	30	b	c	—	10	—	61
4	1a	2c	2	–10	b	d	—	73 ^d	—	—
5	1a	2c	2	–10	c	d	22	—	57	—
6	1a	2c	4	30	b	d	—	17	—	58

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