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

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ARTICLE INFO

 $O = \bigvee_{\substack{N \\ R}}^{n} O + Ar \xrightarrow{Ar} Ar = \frac{1) \text{Zn-TiCl}_4}{2) \text{ cat. } p\text{-TsOH}}$

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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-

> n = 1.2R = Me, H

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)-1H-pyrrol-2(5H)-ones, 6-diarylmethylpyridin-2(1H)-ones, and their hydrogenated analogs.⁴ The reaction mechanisms of the reductive coupling and following reactions are also discussed.

n = 2

Naoki Kise*, Syn Kinameri, Toshihiko Sakurai

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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n = 1.2

two-electron reduced products

n = 1

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



						3	4	5	6	7	8
1	1a	2	0	a	а	18	13	20	32	_	-
2	1a	2	0	a ^d	a	_	_	73	10	_	-
3	1a	2	0	b	а	_	_	80	_	_	-
4	1a	2	0	с	а	18	_	_	61	_	-
5	1a	4	30	a	а	_	_	14	_	31	28
6	1a	4	30	b	а	_	_	12	_	54	-
7	1b	2	0	a	b	10	9	7	30	_	-
8	1b	2	0	b	b	_	_	53	_	_	_
9	1b	2	0	с	b	5	10	_	42	_	-
10	1b	4	30	a	b	_	_	7	_	36	13
11	1b	4	30	b	b	-	—	5	-	47	-

^a $Zn/TiCl_4 = 2/1$.

 b^{-1} (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.

The reaction conditions of the reductive coupling were sur-

veyed with *N*-methylsuccinimide (1a) and benzophenone (2a) as

the substrates and the results are summarized in Table 1.⁵ The molar ratio of $Zn/TiCl_4$ was fixed to 2/1. First, the reduction was car-

ried out with the ratio of $1a/2a/TiCl_4$ 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

^c Isolated yields.

^d 1 M HCl, 25 °C, 3 h.



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

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	с	-	81	_	_	
2	1a	2b	2	0	с	с	-	-	71	-	
3	1a	2b	4	30	b	с	_	10	_	61	
4	1a	2c	2	-10	b	d	_	73 ^d	-	_	
5	1a	2c	2	-10	с	d	22	-	57	-	
6	1a	2c	4	30	b	d	-	17	_	58	

Run	1	2	TiCl ₄ ^a (mmol)	Temp (°C)	Workup ^b		Yield ^c (%)			
							3	5	6	7
7	1b	2b	2	0	b	e	_	53	-	4
8	1b	2b	4	30	b	e	_	9	_	44
9	1b	2c	2	0	b	f	_	49	_	8
10	1b	2c	4	30	b	f	_	4	_	43
11	1b	2d	2	-10	b ^e	g	_	48	_	6
12	1b	2d	4	30	b ^e	g	-	Trace	-	52

Table 2 (continued)

^a Zn/TiCl₄ = 2/1.

^b (b) Cruce product mixture obtained by workup with 1 M HCl 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 Obtained with **9** (8%).

^e Crude product mixture was refluxed in toluene for 2 h.



Scheme 3. Transformation of 6d to 9.

for stirring with 1 M HCl was prolonged to 3 h, the cyclic product **5a** was obtained as the major product (73%) with a small amount of the acyclic product **6a** (run 2). Therefore, the crude product mixture obtained from run 1 was refluxed in the presence of catalytic amount of *p*-TsOH in benzene for 30 min to give **5a** (80%) as the sole product (run 3). In contrast, **6a** was formed mainly (61%) after workup with satd NaHCO₃ aq at 25 °C for 3 h (run 4). Next, the reduction was performed with the ratio of **1a/2a**/TiCl₄ as 1/2/4 in THF at 30 °C for 12 h (runs 5 and 6). After workup with 1 M HCl at 25 °C for 15 min, cyclic product **7a** and acyclic product **8a** were formed as four-electron reduced products (run 5). As expected, **7a** was obtained as the major product (54%) after reflux of the product mixture in benzene similarly to run 3 (run 6). Instead of **1a**, succinimide (**1b**) was employed as the substrate and afforded similar re-

Table 3

Reductive coupling of **10a**,**b** with **2a**–**d** by Zn–TiCl₄



Run	10	10	2	TiCl ₄ ^a (mmol)	Temp (°C)	Workup ^b			Yiel	d ^c (%)		
							11	12	13	14	15	
1	10a	2a	2	0	a	a	_	_	76	_	_	
2	10a	2a	4	30	a	а	_	-	_	_	64	
3	10b	2a	2	0	a	b	33	-	51	_	-	
4	10b	2a	2	0	b	b	_	78	_	_	-	
5	10b	2a	2	30	a	b	_	_	_	12	60	
6	10b	2a	4	30	b	b	_	_	_	72	_	
7	10b	2b	2	0	a	с	54	-	30	_	-	
8	10b	2b	2	0	b	с	-	78	_	_	-	
9	10b	2b	4	30	a	с	_	_	_	16	55	
10	10b	2b	4	30	b	с	_	_	_	68	_	
11	10b	2c	2	0	a	d	_	_	77	6	_	
12	10b	2c	4	30	a	d	_	_	_	15	56	
13	10b	2c	4	30	b	d	_	_	_	70	_	
14	10b	2d	2	0	a	e	70	-	11	_	-	
15	10b	2d	4	30	a	e	_	_	_	13	64	
16	10b	2d	4	30	b	e	-	-	-	75	-	

^a $Zn/TiCl_4 = 2/1$.

^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 toluene in the presence of cat. *p*-TsOH for 2 h. ^c Isolated yields.



Scheme 4. Transformation of 13a and 15a to 12a and 14a

sults (runs 7–11). Although the yields were moderate, cyclic dehydrated products **5b** (53%) and **7b** (47%) could selectively be obtained (runs 8 and 11). While the two-electron reduced products **5a,b** were formed exclusively after reflux in benzene (runs 3 and 8), the four-electron reduced products **7a,b** were obtained as mixtures with small amounts of **5a,b** (runs 6 and 11). Incidentally, these two cyclic products could readily be transformed to each other by reduction with L-Selectride and oxidation with DDQ (Scheme 2). All of the products were determined by spectroscopic⁶ and X-ray crystallographic analyses.⁷

The reductive coupling of **1a,b** with benzophenone derivatives **2b–d** was carried out under the same conditions as those in Table 1 (Table 2). The reaction mixtures obtained from the reductive coupling were refluxed in benzene as described above and cyclic dehydrated products **5** and **7** were obtained selectively in all cases. In the reaction of **1a** with 4,4'-dimethoxybenzophenone (**2c**), a small amount of six-membered cyclized product **9** (8%) was obtained with major five-membered cyclized product **5d** (73%) (run 4). It was confirmed that **9** was selectively produced by reflux in benzene from acyclic product **6d** (Scheme 3); **6d** was prepared by workup with satd NaHCO₃ aq after the reductive coupling (run

5). In the reaction of **1b** with dibenzosuberone (**2d**), the reaction mixtures were refluxed in toluene for 2 h to give **5g** and **7g**, since the cyclization of acyclic products was slow in refluxing benzene (runs 11 and 12).

This reductive coupling was also effective for glutarimides 10a,b in place of 1a,b (Table 3). The reductive coupling of N-methylglutarimide (10a) with 2a was carried out under the same conditions as above (runs 1 and 2). After workup with 1 M HCl, acyclic product 13a (76%) and its deoxygenated product 15a (64%) were formed exclusively. Since cyclization of these acyclic products was slow, a prolonged reaction time was needed even in refluxing toluene (Scheme 4). In the reaction of glutarimide (10b) with 2a (runs 3-6), mixtures of cyclic and acyclic products were formed after workup with 1 M HCl (runs 3 and 5). Reflux of the reaction mixtures in toluene for 2 h gave cyclic dehydrated products 12b (78%) and **14b** (72%), respectively (runs 4 and 6). The reactions of **10b** with other benzophenones **2b–d** also selectively afforded cvclic products **12c** and **14c-e** in moderate to good yields (runs 8, 10, 13, and 16). Acyclic product 13d (77%) and cyclic product 11e (70%) were formed from 2c and 2d, respectively, after workup with 1 M HCl (runs 11 and 14). Unfortunately, the corresponding cyclic dehydrated products 12d and 12e could not be obtained, since the heating of 13d and 11e in cat. p-TsOH/toluene resulted in complex mixtures.

The presumed mechanism of the reductive coupling of **1a** with **2a** is illustrated in Scheme 5. Initially, dianion intermediate **A** is generated by two-electron transfer from low-valent titanium to **2a**. The major by-products are the homo-coupled pinacol and its further reduced McMurry-type alkene, 1,1,2,2-tetraphenylethene. For the cross coupling, the nucleophilic attack of **A** on **1a** forms adduct **B**. The adduct **B** is stable at 0 °C and, therefore, the workup of **B** with water affords diol **3a**. During workup, the dehydration of **3a** is catalyzed under acidic conditions to give **4a** and **5a**, while the ring-opening of **3a** is promoted under basic conditions to lead **6a**. The ring-closing of **6a** to **3a** and subsequent dehydration of **3a** to **5a** through **4a** are effected by reflux in benzene in the presence



Scheme 5. Presumed reaction mechanism of reductive coupling of 1a with 2a by low-valent titanium.

of cat. amount of *p*-TsOH to give **5a** as the sole product eventually. This result suggests that **5a** is thermodynamically the most stable of the four products **3a–6a**. The DFT calculations⁸ at the B3LYP/6-311+G(2d,p) level of the four products also support this result; the relative energies in benzene (PCM) at 353 K are **3a**: 11.6 kcal/mol; **4a**+H₂O: 1.6 kcal/mol; **5a**+2H₂O: –20.1 kcal/mol; **6a**: 0 kcal/mol. On the contrary, the reductive β -elimination of the adduct **B** by low valent titanium is promoted at 30 °C to give **7a**. Alternatively at the elevated temperature, acyclic product **8a** is formed by the ring-opening of **B**, subsequent reduction of resulting **C** to **D**, and then work up of **D** with water. The ring-closing of **8a** and following dehydration to **7a** are also effected by reflux in cat. *p*-TsOH/benzene. DFT calculations⁸ exhibit that **7a** is more stable than **8a**; the relative energies in benzene (PCM) at 353 K are **7a**+H₂O: –3.5 kcal/mol; **8a**: 0 kcal/mol.

In summary, the reductive coupling of succinimides 1a,b and glutarimides 10a,b with benzophenones 2a-d by $Zn-TiCl_4$ gave two- and four-electron reduced products as cyclic and acyclic products. The two- and four-electron reduced products could be prepared selectively by controlling the reaction conditions. The product selectivity of cyclic and acyclic products depends on the employed substrates and the conditions of workup. In most cases, all products were transformed to the corresponding cyclic dehydrated products by heating in the presence of cat. *p*-TsOH. Consequently, five-(5 and 7) and six-membered cyclized products (12 and 14) were synthesized selectively by this method. The application of these compounds is an issue in the future.

Supplementary data

Supplementary data (experimental procedures, characterization data for products, ¹H and ¹³C NMR spectra of products, Xray crystallographic structures, and results of DFT calculations) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.10.053.

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- 4. For the synthesis of the hydrogenated analogs, see: (a) Campaigne, E.; Matthews, D. P. J. Heterocycl. Chem. 1975, 12, 391; (b) Gramain, J.-C.; Remuson, R.; Troin, Y. Tetrahedron 1979, 35, 753.
- 5. Typical procedure for the reductive coupling of 1a with 2a (Table 1, run 1) is as follows. To a solution of 1a (1 mmol), 2a (2 mmol), and zinc powder (4 mmol) in THF (10 mL) was added TiCl₄ (2 mmol) dropwise at 0 °C and then the dark blue suspension was stirred for 12 h at this temperature. To the mixture was added

1 M HCl (20 mL) at 0 °C and the mixture was stirred for 15 min at 25 °C. The mixture was extracted with ethyl acetate three times. The organic layer was washed with aqueous NaCl and dried over MgSO₄. After the solvent was removed, the residue was purified by column chromatography on silica gel to give **3a–6a**.

- 6. See Supplementary data.
- 7 All measurements of X-ray crystallographic analysis were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Ka radiation. The structure was solved by direct methods with SIR-97 and refined with SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the Yadokari-XG software package. Crystal data for 3a, 4a, 5a, 5b, 6a, 7a, 7b, 11b, 12b, and 14b are as follows: CCDC 959918-959927 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/ data_request/cif. Compound 3a (CCDC 959918): C18H19NO3, FW = 297.34, mp 171–172 °C, triclinic, P-1 (no 2), colorless block, a = 9.206(4) Å, b = 12.204(5) Å, c = 15.212(4) Å, α = 69.732(19), β = 85.263(18), γ = 72.399(10), V = 1527.8(9) Å³, T = 298 K, Z = 4, D_{calcd} = 1.293 g/cm³, μ = 0.88 cm⁻¹, GOF = 0.941. Compound **4a** (CCDC 959919): C18H17NO2, FW = 279.33, mp 204-205 °C, triclinic, P-1 (no 2), colorless block, a = 7.897(3) Å, b = 9.993(5) Å, c = 10.888(5) Å, $\alpha = 105.66(4)$, $\beta = 105.03(3), \gamma = 107.33(3), V = 733.9(6) Å^3, T = 298 \text{ K}, Z = 2, D_{\text{calcd}} = 1.264 \text{ g/}$ cm³, $\mu = 0.82$ cm⁻¹, GOF = 1.089. Compound **5a** (CCDC 959920): C₁₈H₁₅NO, FW = 261.31, mp 121-122 °C, monoclinic, P21/c (no 14), yellow block, a = 10.54(2)Å, b = 17.82(4)Å, c = 15.22(2)Å, $\beta = 87.88(16)$, V = 2857(9)Å³, T = 298 K, Z = 8, $D_{calcd} = 1.215$ g/cm³, $\mu = 0.75$ cm⁻¹, GOF = 0.876. Compound **5b** (CCDC 959921): C₁₇H₁₃NO, FW = 247.28, mp 189–191 °C, monoclinic, P2₁/a (no 14), yellow block, a = 9.969(3) Å, b = 10.2341(18) Å, c = 12.943(4) Å, $\beta = 93.333(6)$, $V = 1318.2(6) \text{ Å}^3$, T = 298 K, Z = 4, $D_{\text{calcd}} = 1.246 \text{ g/cm}^3$, $\mu = 0.78 \text{ cm}^{-1}$, GOF = 1.027. Compound **6a** (CCDC 959922): C₁₈H₁₉NO₃, FW = 297.34, mp 168-169 °C, monoclinic, $P2_1/a$ (no 14), colorless block, a = 15.152(5) Å, b = 10.429(6) Å, c = 14.911 (8) Å, $\beta = 42.328(15)$, $\nu = 1586.6(13)$ Å³, T = 298 K, Z = 4, $D_{calcd} = 1.245$ g/cm³, $\mu = 0.85$ cm⁻¹, GOF = 1.077. Compound **7a** (CCDC 959923): $C_{18}H_{17}NO$, FW = 263.33, mp 133 °C, monoclinic, $P2_{1/c}$ (no 14), colorless block, $T = 298 \text{ K}, Z = 8, D_{\text{calcd}} = 1.232 \text{ g/cm}^3, \mu = 0.76 \text{ cm}^{-1}, \text{ GOF} = 1.029. \text{ Compound } \mathbf{7b}$ (CCDC 959924): $C_{17}H_{15}NO$, FW = 249.30, mp 187–188 °C, triclinic, P-1 (no 2), colorless block, a = 7.136(3) Å, b = 7.914(3) Å, c = 12.230(4) Å, $\alpha = 90.35(2)$, $\mu = 0.77 \text{ cm}^{-1}$, GOF = 1.067. Compound **11b** (CCDC 959925): C₁₈H₁₇NO₂, FW = 279.33, mp 178–179 °C, triclinic, *P*-1 (no 2), colorless block, *a* = 5.982(3) Å, *b* = 14.544(6) Å, *c* = 18.251(8) Å, *α* = 73.67(4), *β* = 82.65(4), *γ* = 78.89(3), *V* = 1490.5(11) Å³, *T* = 298 K, *Z* = 4, $D_{calcd} = 1.245 \text{ g/cm}^3$, *μ* = 0.81 cm⁻¹, GOF = 0.893. Compound **12b** (CCDC 959926): C₁₈H₁₅NO, FW = 261.31, mp 215– $\gamma = 78.89(3),$ 217 °C, triclinic, P-1 (no 2), colorless block, a = 7.973(16) Å, b = 9.220(20) Å, c = 10.492(20) Å, $\alpha = 65.07(18)$, $\beta = 75.19(17)$, $\gamma = 75.8(2)$, V = 668(2) Å³, T = 298 K, Z = 2, $D_{calcd} = 1.299 \text{ g/cm}^3$, $\mu = 0.80 \text{ cm}^{-1}$, GOF = 1.097. Compound **14b** (CCDC 959927): $C_{18}H_{17}NO$, FW = 263.33, mp 153–154 °C, monoclinic, P2₁ (no 4), V = 704.2(3) Å³, T = 298 K, Z = 2, $D_{calcd} = 1242$ g/cm³, $\mu = 0.77$ cm⁻¹, GOF = 1.044.
- 8. All DFT calculations were carried out with the GAUSSIAN 09⁹ program. Geometry optimization was performed at the B3LYP/6-311+G(2d,p) level using the IEFPCM models for benzene solvent to take the solvent effect into consideration. The optimized geometries were verified by the vibrational analysis and their energies were thermally corrected to 353 K based on the frequencies. For optimized structures of 3a-8a, see Supplementary data.
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