

Reductive Coupling of 2-Propyn-1-ones Promoted by Yb Metal or YbCl₃-Zn

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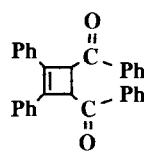
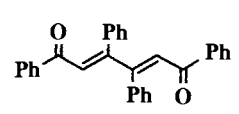
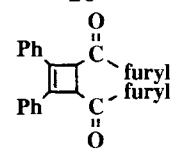
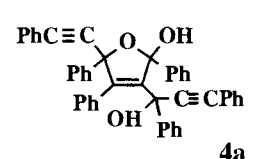
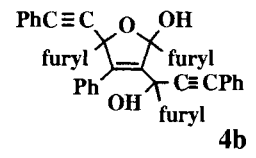
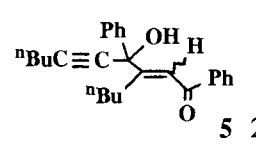
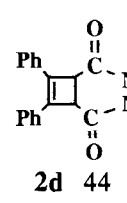
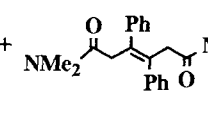
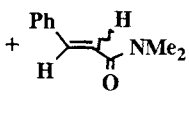
Ytterbium metal promotes reductive coupling of 2-propyn-1-ones (**1**) to give cyclobutenes and 1,6-dioxo-2,4-hexadiene, whereas **1** is converted to 2,5-dihydrofurans on the treatment with YbCl₃-Zn

Coupling reaction of alkynes with aldehydes promoted by low-valent d-block transition metals, particularly niobium¹⁾ and tantalum²⁾ has been a versatile method for the synthesis of tri- and tetra-substituted olefinic compounds. However little is known about this approach using f-block metals, although some alkyne-lanthanoid complexes are well characterized.³⁾ In the previous paper, we have demonstrated a facile reductive dimerization of α,β -unsaturated carbonyl compounds by ytterbium metal to yield cyclopentanol.⁴⁾ Furthermore this reaction was promoted more stereoselectively by the YbCl₃-Zn system.⁵⁾ We report herein a reductive coupling reaction of 2-propyn-1-ones by low-valent ytterbium.

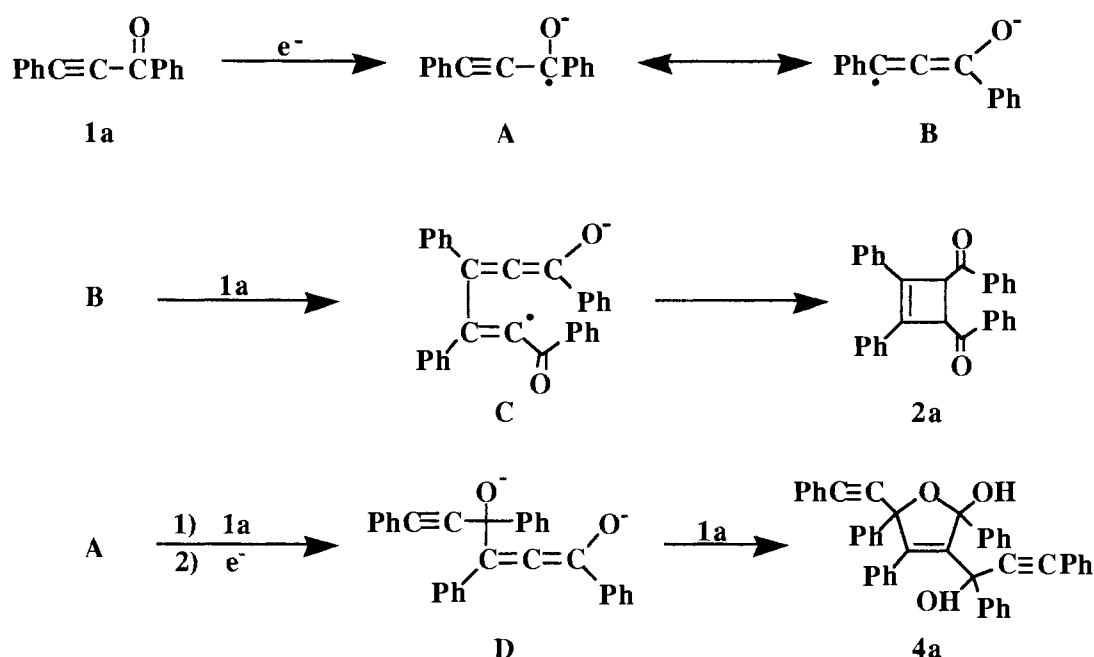
Treatment of 1,3-diphenyl-2-propyn-1-one (**1a**) with Yb metal in THF-HMPA at 0 °C gave 3,4-dibenzoyl-1,2-diphenylcyclobutene (**2a**) in 36% yield (Table 1). The product **2a** was obtained as a single isomer, but its stereochemistry was not determined.⁶⁾ When the reaction was carried out at -78 °C, linear dimer, 1,6-dioxo-2,4-hexadiene, **3** was isolated in 46% yield along with **2a**. 2-Propyn-1-one **1b** was also changed to cyclobutene **2b** on the treatment with Yb metal at 0 °C, though the yield was decreased because of formation of polymeric products.

Next we examined the reaction using YbCl₃-Zn in order to improve the yield.⁵⁾ Surprisingly, **1a** was converted to three stereoisomers of 2,5-dihydrofuran **4a** in 72% total yield,⁷⁾ and dimers corresponding to **2** and **3** were not detected.⁸⁾ Similarly the reaction of **1b** also gave trimer **4b** in 23% yield. In contrast, enyne dimer **5** was obtained by the treatment of **1c** with the reagent. Reaction of *N,N*-dimethylphenylpropiolamide (**1d**) with YbCl₃-Zn under reflux for 21 h gave cyclobutene **2d**, dimeric amide **6**, and cinnamamide **7** in 44%, 8%, and 9% yields, respectively.

Table 1. Reductive Coupling of 2-Propyn-1-ones by Yb Metal or YbCl₃-Zn

Substrate	Method ^{a)}	Temp/°C	Time/h	Product and Yield/% ^{b)}
$\text{PhC}\equiv\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CPh}$ 1a	A	0	2.5	 2a 36
1a	A	-78	24	2a +  3 46 ^{c)}
$\text{PhC}\equiv\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{C}(\text{furyl})_2$ 1b	A	0	5.5	 2b 9
1a	B	0	6	 4a 72 ^{d)}
1b	B	r.t.	18	 4b 23 ^{e)}
$^n\text{BuC}\equiv\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CPh}$ 1c	B	0	6	 5 20(62) ^{f)}
$\text{PhC}\equiv\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CNMe}_2$ 1d	B	reflux	21	 2d 44 +  6 8 ^{c)} +  7 9 ^{g)}

a) Method A: substrate (2.5 mmol); Yb (1 mmol); THF (4 ml)-HMPA (1 ml). Method B: substrate (1 mmol); YbCl₃ (1 mmol)-Zn (1.5 mmol); THF (7 ml). b) Isolated yield (GC yield) based on Yb for method A or based on the substrate for method B. c) Undetermined single isomer d) Three stereoisomers were isolated in 59%, 8%, and 5% yields, respectively. e) A mixture of two stereoisomers (60:40). f) A mixture of cis and trans (50:50). g) Trans (5%) and cis (4%) were isolated.



Scheme 1.

Formation of the products is plausibly accounted for as follows (Scheme 1). The 2-propyn-1-one **1a** was reduced with low-valent ytterbium to ketyl **A** and radical enolate **B**. In the reaction with Yb metal, radical addition of **B** to **1a** gave tail-to-tail dimer **C**, whose protonation at low temperature led to the hexadiene **3** and cyclization followed by isomerization afforded the cyclobutene **2a**, respectively. On the other hand, contribution of the ketyl **A** was important in the reaction with YbCl₃-Zn. 1,4-Addition of **A** to **1a** and subsequent reduction yielded head-to-tail dimer **D**,⁹⁾ which was finally converted to the dihydrofuran **4a** by the reaction with **1a** followed by Yb(III)-catalyzed ketalization.¹⁰⁾ The factors to control the two reaction paths are not clear at present.

Thus, the reductive coupling of 2-propyn-1-ones affords mainly cyclobutenes or dihydrofuran derivatives, depending on the choice of the ytterbium reagents.

A typical example is as follows: (method B) a slurry of anhydrous YbCl₃ (280 mg, 1 mmol) and Zn (98 mg, 1.5 mmol) in THF (4 ml) was stirred under N₂ at room temperature until grayish color changed to green (~3 h). Then 2-propyn-1-one **1a** (206 mg, 1 mmol) in THF (3 ml) was added to the mixture at 0 °C and stirred for 6 h. The reaction was quenched with 2*N* HCl. After usual work-up, column chromatography on silica gel gave three stereoisomers of 2,5-dihydrofuran **4a** (122 mg, 59%; 11 mg, 5%, and 17 mg, 8%).

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References

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- 6) **2a**: white needles; mp 195-197 °C; IR (Nujol) 1682 (CO) cm^{-1} ; MS (70 eV) m/e 414 (M^+), 309 ($\text{M}^+ - \text{PhCO}$), 105 (PhCO^+); $^1\text{H-NMR}$ (CDCl_3) δ 5.32 (2H, s), 7.12-7.52 (18H, m), 7.70-7.80 (2H, m); $^{13}\text{C-NMR}$ (CDCl_3) δ 51.2 (C_3 and C_4), 127.1, 128.1, 128.2, 132.8, 134.0, 137.1, 139.7 (C_1 and C_2), 196.7 (CO). Anal. Found: C, 86.90; H, 5.30%. Calcd for $\text{C}_{30}\text{H}_{22}\text{O}_2$: C, 86.93; H, 5.35%.
- 7) **4a** (major): yellow oil: IR (neat) 3355 (OH), 2222 ($\text{C}=\text{C}$) cm^{-1} ; MS (70eV) m/e 620 (M^+), 603 ($\text{M}^+ - \text{OH}$), 497 (603- PhCOH^+), 105 (PhCO^+); $^1\text{H-NMR}$ (CDCl_3) δ 3.50 (1H, s, OH), 4.23 (1H, s, OH), 6.94-7.78 (30H, m); $^{13}\text{C-NMR}$ (CDCl_3) δ 71.3 (COH), 87.4, 87.9, 88.8, 89.8 ($\text{C}=\text{C}$), 91.5 (C_5), 111.0 (C_2), 122.0, 126.0, 126.6, 126.7, 126.9, 127.0, 127.1, 127.2, 127.4, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 130.6, 131.4, 131.5, 131.6, 138.2, 141.1, 142.1, 144.9. Anal. Found: C, 86.97; H, 5.10%. Calcd for $\text{C}_{45}\text{H}_{32}\text{O}_3$: C, 87.07; H, 5.19%.
- 8) Most amount of **1a** was recovered unchanged on the treatment with Zn under similar conditions.
- 9) Alternatively, **1a** may be reduced to dianion, which reacts further with **1a** to give the dimer **D**.
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