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Reductive Coupling of 2-Propyn-1-ones Promoted by Yb Metal or $YbCl_3$-Zn

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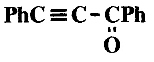
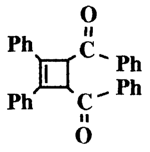
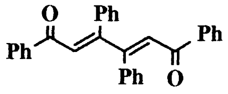
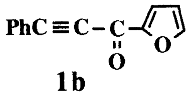
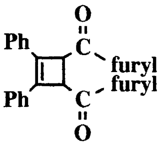
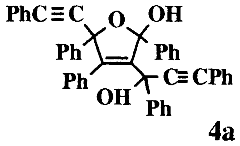
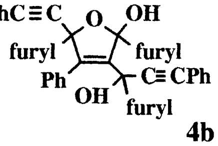
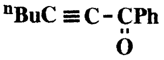
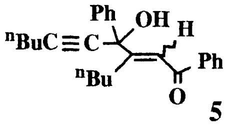
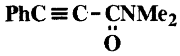
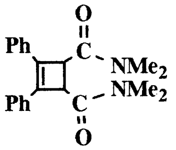
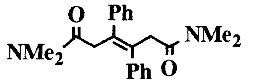
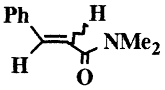
Ytterbium metal promotes reductive coupling of 2-propyn-1-ones (**1**) to give cyclobutenes and 1,6-dioxo-2,4-hexadiene, whereas **1** is converted to 2,5-dihydrofurans on the treatment with $YbCl_3$-Zn

Coupling reaction of alkynes with aldehydes promoted by low-valent d-block transition metals, particularly niobium$^{1)}$ and tantalum$^{2)}$ 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 cyclopentanols.$^{4)}$ Furthermore this reaction was promoted more stereoselectively by the $YbCl_3$-Zn system.$^{5)}$ We report herein a reductive coupling reaction of 2-propyn-1-ones by low-valent ytterbium.

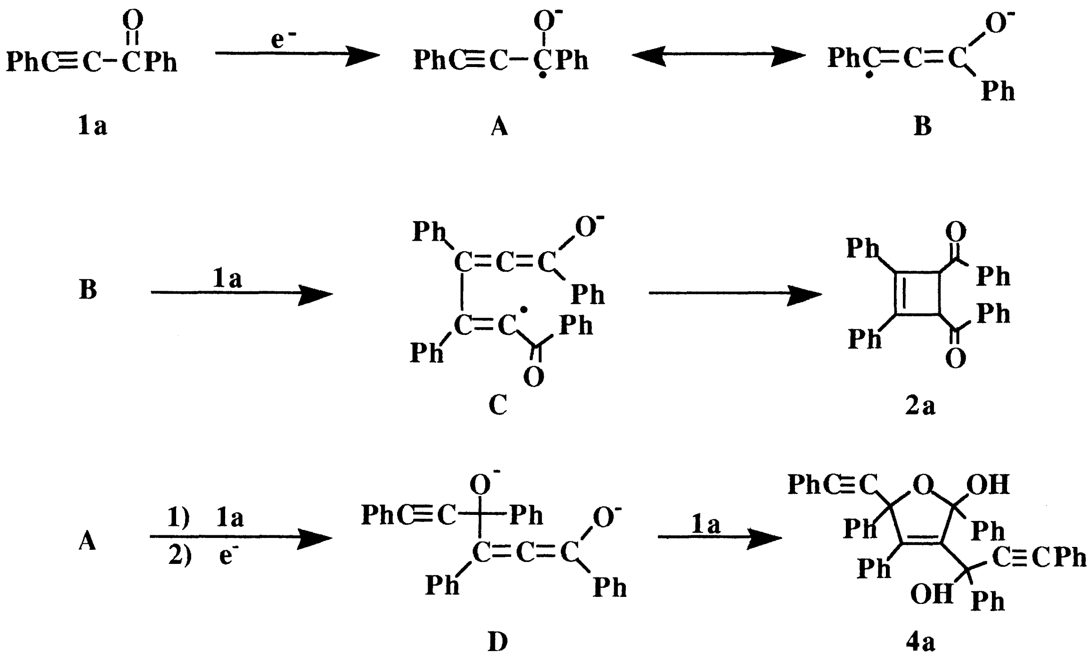
Treatment of 1,3-diphenyl-2-propyn-1-one (**1a**) with Yb metal in THF-HMPA at 0 °C gave 3,4-dibenzoyl-1,2-diphenylcyclobutene (**2a**) in 36% yield (Table 1). The product **2a** was obtained as a single isomer, but its stereochemistry was not determined.$^{6)}$ When the reaction was carried out at -78 °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 $YbCl_3$-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 $YbCl_3$-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 $YbCl_3$-Zn

Substrate	Method[a]	Temp/°C	Time/h	Product and Yield/%[b]
 $\mathrm{PhC{\equiv}C{-}\underset{\underset{O}{\|}}{C}Ph}$ 1a	A	0	2.5	 2a 36
1a	A	-78	24	2a +  28 3 46[c]
 1b	A	0	5.5	 2b 9
1a	B	0	6	 4a 72[d]
1b	B	r.t.	18	 4b 23[e]
 $\mathrm{{}^{n}BuC{\equiv}C{-}\underset{\underset{O}{\|}}{C}Ph}$ 1c	B	0	6	 5 20(62)[f]
 $\mathrm{PhC{\equiv}C{-}\underset{\underset{O}{\|}}{C}NMe_2}$ 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); $YbCl_3$ (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 $YbCl_3$-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 $YbCl_3$ (280 mg, 1 mmol) and Zn (98 mg, 1.5 mmol) in THF (4 ml) was stirred under N_2 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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5) K.Takaki, K.Nagase, F.Beppu, and Y.Fujiwara, submitted.
6) **2a**: white needles; mp 195-197 °C; IR (Nujol) 1682 (CO) cm^{-1}; MS (70 eV) m/e 414 (M^+), 309 (M^+-PhCO), 105 ($PhCO^+$); ^{1}H-NMR ($CDCl_3$) δ 5.32 (2H, s),7.12-7.52 (18H, m), 7.70-7.80 (2H, m); ^{13}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 $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%.
7) **4a** (major): yellow oil: IR (neat) 3355 (OH), 2222(C≡C) cm^{-1}; MS (70eV) m/e 620 (M^+), 603 (M^+-OH), 497 (603-$PhCOH^+$), 105 ($PhCO^+$); ^{1}H-NMR ($CDCl_3$) δ 3.50 (1H, s, OH), 4.23 (1H, s, OH), 6.94-7.78 (30H, m); ^{13}C-NMR ($CDCl_3$) δ 71.3 (COH), 87.4, 87.9, 88.8, 89.8 (C≡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 $C_{45}H_{32}O_3$: 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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