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Preparation and Reactions of γ,γ-Dialkoxyallylic Zirconium Species: α,β-Unsaturated Acyl Anion Equivalent

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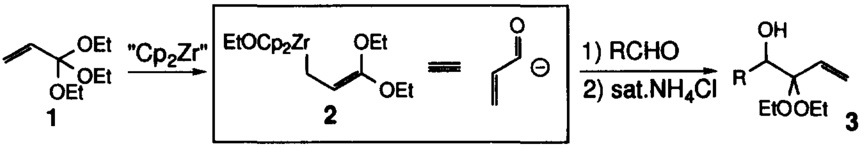
Abstract: γ,γ-Dialkoxyallylic zirconium species can be easily prepared from the reaction of triethyl orthoacrylate with zirconocene eqivalent (zirconocene-butene complex). This species reacts with aldehydes as an α,β-unsaturated acyl anion equivalent to give the 1-substituted-2,2-diethoxy-3-buten-1-ol derivatives. © 1997 Elsevier Science Ltd.

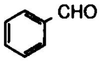
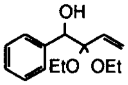
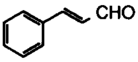
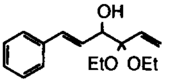
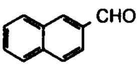
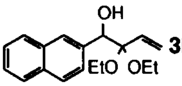
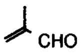
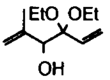
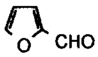
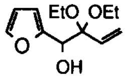
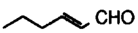
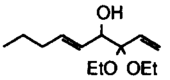
α,β-Unsaturated carbonyl moiety is well documented as one of the fundamental group in organic synthesis because of its potential and useful reactivities in various reactions. Related to this chemistry, synthetic equivalents of α,β-unsaturated acyl anion synthon have been developed, mainly based on heteroatom containing allylic or allenic organometallics.[1,2] We have recently reported the practical preparative method of allylic zirconium species from allylic ethers with zirconocene equivalent (zirconocene-butene complex, "Cp_2Zr")[3] through the formation of zirconacyclopropane and following β-elimination of alkoxyl group.[4] This process would be applicable to generate the γ,γ-dialkoxyallylic zirconium species from orthoacrylate derivative. We report herein that γ,γ-bisalkoxyallylic zirconium species **2** can be conveniently prepared by the reaction of triethyl orthoacrylate (**1**) with "Cp_2Zr". This species, which acts as a synthetic equivalent of α,β-unsaturated acyl anion synthon reacted with aldehydes in regioselective manner to afford the 1-substituted-2,2-diethoxy-3-buten-1-ol derivatives **3** (Scheme 1).

Scheme 1



The preparation and reactions of γ,γ-dialkoxyallylic zirconium species are summarized in Table 1. The reaction of triethyl orthoacrylate (**1**)[5] with *in situ* generated "Cp_2Zr" and following addition of benzaldehyde proceeded smoothly to give 1-phenyl-2,2-diethoxy-3-buten-1-ol (**3a**).[6] With other aromatic aldehyde (2-naphthaldehyde and furfural, entries 2,3), the corresponding hydroxy acetal derivatives **3b** and **3c** were obtained in exellent yields, while with α,β-unsaturated aldehydes (entries 4-6), **3d**, **3e**, and **3f** were obtained in 58-90 % yields. The reaction with 3-phenylpropionaldehyde or dibenzalacetone gave a complex mixture along with a trace amount of **3**. When **3a** and **3d** were treated with 50 % aqueous CF_3CO_2H in $CHCl_3$, the corresponding keto forms were obtained in 90 % and 84 % yield, respectively.

Table 1. The reaction of γ,γ-dialkoxyallylic zirconium species with aldehydes

Entry	Aldehyde	Product		Yield (%)[a]	Entry	Aldehyde	Product		Yield (%)[a]
1			3a	91	4			3d	90
2			3b	96	5			3e	58
3			3c	90	6			3f	66

[a] Isolated yield.

To confirm the formation of γ,γ-dialkoxyallylic zirconium species **2**, we examined the ^{1}H NMR study of the intermediate. After treating of **1** with "Cp_2Zr" in toluene at room temperature, the solvent was changed to benzene-d_6 and the ^{1}H NMR was measured. An olefinic and methylene protons appeared at 4.50 ppm (1H, t, J = 8.7 Hz) and 1.97 ppm (2H, d, J = 8.7 Hz), respectively. Three methylene peaks of ethoxy groups appeared at 4.04, 3.91, and 3.80 ppm. The observed spectrum is possibly supporting the existence of γ,γ-dialkoxyallylic zirconium species **2**.

We described here the new preparative method of γ,γ-dialkoxyallylic zirconium species from triethyl orthoacrylate with "Cp_2Zr". This species behaved as the α,β-unsaturated acyl anion equivalent in the reaction with aromatic and α,β-unsaturated aldehydes. Preparation of chiral γ,γ-dialkoxyallylic zirconium species and its application to asymmetric synthesis are currently carried out.

References and Notes

1. Reviews of α,β-unsaturated acyl anion equivalent based on the heteroatom stabilized allylic and allenic anions; a) Yamamoto, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 1.2. b) Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 1.3.
2. γ,γ-Dialkoxyallylic lithium species; Seyferth, D.; Mammarella, R. E.; Klein, H. A. *J. Organomet. Chem.* **1980**, *194*, 1-7.
3. Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829-2832.
4. a) Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 1295-1298. b) Ito, H.; Nakamura, T.; Taguchi, T.; Hanzawa, Y. *Tetrahedron* **1995**, *51*, 4507-4518.
5. Triethyl orthoacrylate can be easily prepared from commercially available triethyl orthopropionate through bromination (Br_2, pyridine) and following elimination (t-BuOK). The detail of preparative procedure was according to the following literature: Stetter, H.; Uerdingen, W. *Synthesis* **1973**, 207-208.
6. Typical experimental procedure is as follows: A solution of triethyl orthoacrylate (174 mg, 1mmol) in toluene (2 mL) was added to a solution of "Cp_2Zr" (1.2 mmol), prepared from Cp_2ZrCl_2 with n-BuLi[3,4] at -78 °C. After stirring for 3 h at room temperature, a solution of benzaldehyde (159 mg, 1.5 mmol) in toluene (2 mL) was added at -78 °C and stirred at room temperature for 3 h. After neutral workup (NH_4Cl aq.) and purification with silica gel column chromatography, the product **3a** was obtained (215 mg, 0.91 mmol, 91 %).

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