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Journal of Organometallic Chemistry 575 (1999) 76–79

Journal of Organometallic Chemistry

Oxovanadium(V)-induced oxidation of alkenylzirconocenes for facile inter- and intramolecular coupling

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Received 11 August 1998; received in revised form 11 September 1998

Abstract

The oxidation reaction of (*E*)-1-alkenylchlorozirconocenes with an oxovanadium(V) compound at room temperature led to intermolecular homocoupling, giving the corresponding (*E*,*E*)-dienes stereoselectively. (*E*)-1-Alkenyl-1-alkynylzirconocenes underwent the oxovanadium(V)-induced intramolecular cross-coupling of organic substituents on zirconium, leading to the stereoselective formation of the (*E*)-enynes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Oxovanadium; Organozirconocene compound; Hydrozirconation; Oxidative coupling

1. Introduction

Organozirconocene derivatives that can be prepared easily by hydrozirconation of alkynes and alkenes are useful intermediates in organic syntheses [1]. For example, alkenylzirconocenes are utilized widely as precursor organometallics in the coupling reactions via transmetallation, as represented by the CuCl-induced coupling to (*E*,*E*)-dienes [1–3]. Besides the transformations via transmetallation, the reductive elimination via one-electron oxidation is known to occur with the electron-poor, zero-valent organozirconocenes [4]. The choice of metallic oxidants is a key to achieve such an oxidative transformation, and oxovanadium(V) compounds are promising as candidates for this transformation, because their properties as Lewis acids with one-electron oxidation capability make oxovanadium(V) compounds fascinating as selective oxidants in organic synthesis [5,6]. Thus, we investigated the oxidation of alkenylzirconocene derivatives with oxovanadium(V) compounds.

2. Results and discussion

Treatment of 1-alkenylchlorozirconocene **1**, produced by hydrozirconation of 1-alkyne, with an oxovanadium(V) compound at room temperature led to intermolecular coupling, giving the corresponding (*E*,*E*)-diene **2** stereoselectively (Eq. (1)). Use of two or three equivalents of $VO(O^iPr)_2Cl$ raised the yield of **2** (Table 1, entries 1–3). The yield of **2** was lowered by the use of $VO(OEt)Cl_2$, which is a stronger oxidant than $VO(O^iPr)_2Cl$ (entries 4–5). This is most probably due to further oxidation of **2** by $VO(OEt)Cl_2$, and the reaction at −78°C improved the yield of **2** dramatically (entry 6). Similarly, several 1-alkynes were converted to the expected 1,3-dienes **2** stereoselectively in good yields under the same conditions as those carried out in the entry 3 (three equivalents of $VO(O^iPr)_2Cl$, room temperature, entries 7–9).

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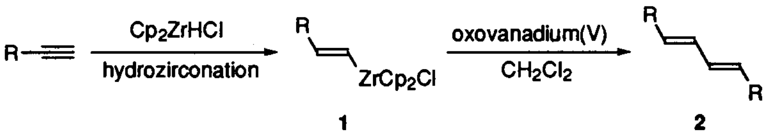
PII: S0022-328X(98)00978-4



(1)

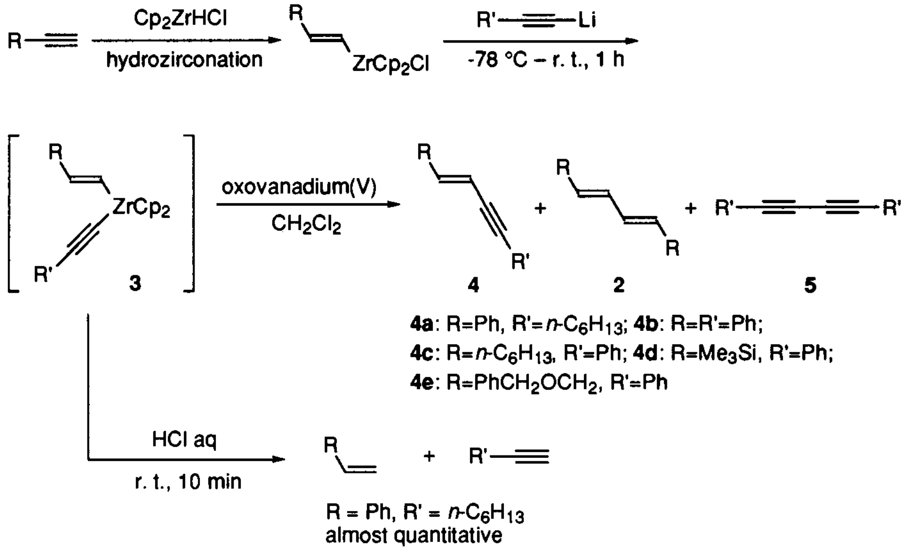
The substitution of the 1-alkenylchlorozirconocene **1** with 1-alkynyllithium at −78°C, followed by treatment with $VO(O^{i}Pr)_2Cl$ led to a novel cross-coupling of organic substituents on zirconium, giving the corresponding *trans*-enyne **4** stereoselectively (Scheme 1, Table 2). The use of $VO(OEt)Cl_2$, again, decreased the yield of **4** from the same reason mentioned above (entries 2–3). Although stoichiometric or excess amounts of $VO(O^{i}Pr)_2Cl$ are required for this transformation, this method was applicable to other combinations of **1** and 1-alkynyllithiums giving *trans*-enynes **4** in moderate to good yields under the similar conditions as indicated in entry 1 (entries 4–6).

Although the reaction pathway for this coupling reaction is ambiguous, the following observations present some information. Negishi and his coworkers reported 1,2-migration in the reaction of Cp_2ZrCl_2 with three equivalents of lithium acetylide to afford the enyne and diyne upon treatment with HCl(aq.) and I_2, respectively, via the intermediate **8** (Scheme 3) [7]. We investigated the similar reaction of **1a** with two equivalents of lithium phenylacetylide, which gave the diene **7** by treatment with HCl(aq.) (Scheme 2). In contrast to this finding, the equimolar reaction of **1a** with 1-octynyllithium gave only styrene and 1-octyne after treatment with HCl(aq.) (Scheme 1). These results suggest the involvement of the different organozirconium intermediates in each reaction. In the former case using two equivalents of lithium phenylacetylide, oxidation with $VO(OEt)Cl_2$ was found to provide the enyne **4b** in good yield, proba-

Table 1
Oxidative homocoupling of alkenylchlorozirconocene **1**

Entry	1	R	Oxovanadium	Equivalent	Conditions	2	%[a]
1	**1a**	Ph	$VO(O^{i}Pr)_2Cl$	1	r.t., 18 h	**2a**	34
2	**1a**	Ph	$VO(O^{i}Pr)_2Cl$	2	r.t., 18 h	**2a**	52
3	**1a**	Ph	$VO(O^{i}Pr)_2Cl$	3	r.t., 18 h	**2a**	91
4	**1a**	Ph	$VO(OEt)Cl_2$	1	r.t., 18 h	**2a**	26
5	**1a**	Ph	$VO(OEt)Cl_2$	3	r.t., 18 h	**2a**	42
6	**1a**	Ph	$VO(OEt)Cl_2$	3	−78°C, 1 h	**2a**	90
7	**1b**	n-C_6H_{13}	$VO(O^{i}Pr)_2Cl$	3	r.t., 18 h	**2b**	88
8	**1c**	Me_3Si	$VO(O^{i}Pr)_2Cl$	3	r.t., 18 h	**2c**	80
9	**1d**	$PhCH_2OCH_2$	$VO(O^{i}Pr)_2Cl$	3	r.t., 18 h	**2d**	55

[a] Isolated yield.



Scheme 1.

bly via the intermediate **6** formed by 1,2-migration (Scheme 2). However, in the latter case, the intermediate **3** is assumed to be involved in the equimolar reaction of **1a** with 1-alkynyllithium, allowing to the oxidative transformation to **4**.

The present reactions widen the scope of organozirconium compounds in organic synthesis. One-electron oxidative transformations of organometallics such as aluminum [8], boron [9], and zirconium provides a versatile synthetic tool for the carbon–carbon bond formation via coupling.

3. Experimental

^{1}H-NMR or ^{13}C-NMR spectra were recorded on a JEOL JNM-GSX-400 spectrometer (400 MHz) and a Varian MERCURY 300 spectrometer (300 MHz) in chloroform-*d* with tetramethylsilane or residual chloroform as an internal standard. Mass spectra were recorded on a Varian SATURN3 and JEOL JMS-DX-303. GC analysis was carried out on a SHIMADZU GC-8A. Infrared spectra were recorded on a Perkin-Elmer 1600. Melting points were determined on a Yanagimoto Micromelting Point Apparatus. Isolation of products by GPC was carried out on an LC-08 of the Japan Analytical Industry. All solvents were dried and distilled. The benzyl ether derivative **1d** was prepared according to the standard procedure [10]. $VO(OEt)Cl_2$ and $VO(O^iPr)_2Cl$ were obtained easily from $VOCl_3$ and the corresponding alcohol, and then distilled [11].

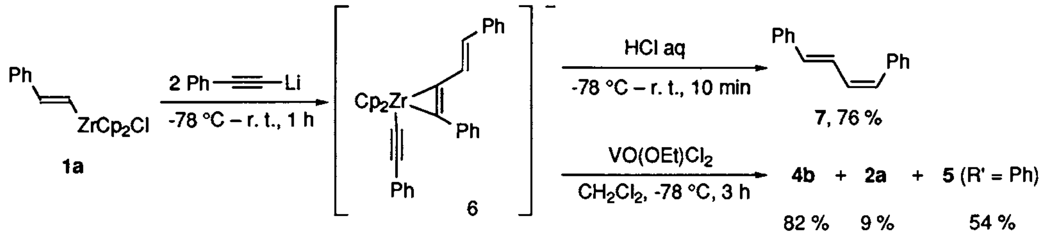
3.1. General procedure for oxidative coupling of alkenylchlorozirconocene 1

To a stirred solution of Cp_2ZrHCl (1.0 mmol, 258 mg) in dry dichloromethane (4 ml) at room temperature under argon, 1-alkyne (1.0 mmol) was added to generate the 1-alkenylzirconocene **1**. After stirring for 1 h at room temperature, $VO(O^iPr)_2Cl$ (660 mg, 3.0 mmol) was added dropwise to the resulting solution over 10 min at 0°C. The mixture was stirred for 18 h at room temperature, and then ether (15 ml) and 1.5 M aqueous HCl (1 ml) were added to the reaction mixture. After extraction with ether (3 × 10 ml), the combined ethereal solution was washed with saturated NH_4Cl, saturated $NaHCO_3$, and brine. The organic

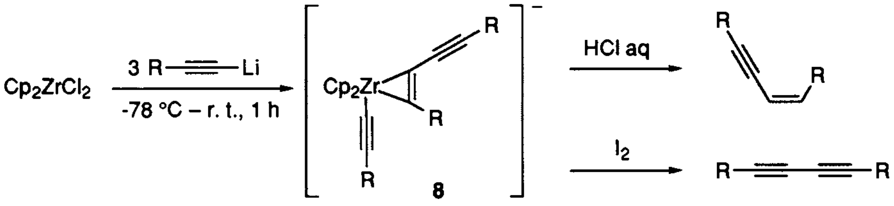
Table 2
Oxidative cross-coupling of alkenylalkynylzirconocene **3**

Entry	R	R′	Oxovanadium	Conditions	%[a]		
					4	**2**	**5**
1	Ph	n-C_6H_{13}	$VO(O^iPr)_2Cl$	r.t., 18 h	64	15	28
2	Ph	n-C_6H_{13}	$VO(OEt)Cl_2$	r.t., 18 h	30	14	27
3	Ph	Ph	$VO(OEt)Cl_2$	−78°C, 3 h	63	14	27
4	n-C_6H_{13}	Ph	$VO(O^iPr)_2Cl$	r.t., 18 h	62	17	25
5	Me_3Si	Ph	$VO(O^iPr)_2Cl$	r.t., 18 h	70	6	22
6	$PhCH_2OCH_2$	Ph	$VO(O^iPr)_2Cl$	r.t., 18 h	57	10	24

[a] Isolated yield.



Scheme 2.



Scheme 3.

layer was dried over $MgSO_4$, and concentrated. Purification by chromatography on a silica-gel column eluting with hexane–chloroform gave the 1,3-diene **2** as shown in Table 1.

2d: $R_f = 0.20$ (hexane–chloroform v/v 1:1). IR (NaCl) 3028, 2852, 1495, 1453, 1359, 1099, 991, 736, 697 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38–7.26 (m, 10H), 6.38–6.24 (m, 2H), 5.92–5.74 (m, 2H), 4.53 (s, 4H), 4.08 (d, $J = 5.7$ Hz, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 138.1, 131.9, 129.8, 128.3, 127.6, 127.5, 72.1, 70.2. Anal. Calc. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.38; H, 7.27.

*3.2. General procedure for oxidative coupling of alkenylalkynylzirconocene **3***

To a solution of Cp_2ZrHCl (1.0 mmol, 258 mg) in dry dichloromethane (4 ml), 1-alkyne (1.0 mmol) was added at room temperature under argon. After stirring for 1 h at room temperature, a solution of 1-alkynyllithium (1.0 mmol) in dry ether (3 ml) was added via cannula to the thus obtained 1-alkenylzirconocene at −78°C. The solution was warmed to room temperature and stirred for an additional 1 h. The reaction mixture was added via cannula to a solution of $VO(O^iPr)_2Cl$ (660 mg, 3.0 mmol) in dichloromethane (4 ml) at 0°C. After stirring for another 18 h at room temperature, and then ether (15 ml) and 1.5 M aqueous HCl (1 ml) were added to the reaction mixture. After extraction with ether (3 × 10 ml), the combined ethereal solution was washed with saturated NH_4Cl, saturated $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, and concentrated. The crude product was purified by a silica-gel column chromatography eluting with hexane–chloroform or GPC to give the *trans*-enyne **4**.

4d: $R_f = 0.25$ (hexane). IR (NaCl) 2956, 1568, 1489, 1249, 974, 840 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.35–7.28 (m, 3H), 6.55 (d, $J = 19.2$ Hz, 1H), 6.18 (d, $J = 19.2$ Hz, 1H), 0.19 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.8, 132.7, 131.6, 128.3, 128.2, 123.3, 89.8, 89.6, −1.7. Anal. Calc. for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 77.62; H, 8.45.

4e: $R_f = 0.30$ (hexane–chloroform v/v 2:1). IR (NaCl) 3030, 2846, 1489, 1360, 1115, 953, 756, 690 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.40–7.28 (m, 8H), 6.33 (dt, $J = 16.2$ Hz, $J = 5.5$ Hz, 1H), 6.02 (dt, $J = 16.2$ Hz, $J = 1.8$ Hz, 1H), 4.57 (s, 2H), 4.14 (dt, $J = 5.5$ Hz, $J = 1.8$ Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.4, 138.0, 131.5, 128.4, 128.3, 128.2, 127.7, 127.7, 123.2, 111.7, 90.0, 87.4, 72.3, 69.8. Anal. Calc. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.12; H, 6.70.

Acknowledgements

The use of the facilities of the Analytical Center, Faculty of Engineering, Osaka University is acknowledged. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan.

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