J. Org. Chem. **1990**, *55*, 1707-1708

Tantalum–Alkyne Complexes as Synthetic Intermediates. Stereoselective Preparation of Trisubstituted Allylic Alcohols from Acetylenes and Aldehydes

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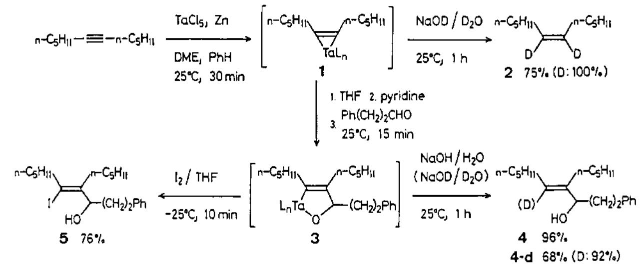
Received December 18, 1989

Summary: A variety of tantalum–alkyne complexes have been generated (but not isolated) by treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc. These complexes add to carbonyl compounds in a one-to-one fashion to yield (*E*)-allylic alcohols, regio- and stereoselectively.

Transition metal–alkyne complexes have received much attention recently, both because of their unique properties and usefulness as synthetic intermediates. In contrast to the Group IV metals such as Ti[1] and Zr,[2] Group V metal–alkyne complexes have not been widely utilized in organic synthesis.[3] Low-valent tantalum complexes react with inactivated acetylenic triple bonds to form tantalum–alkyne complexes.[4-8] Because they are sterically congested, the only carbon–carbon bond forming transformations which have been effected using these complexes are cyclotrimerizations.[7,8] We disclose herein (i) that a variety of tantalum–alkyne complexes have been generated (but not isolated) by treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc, (ii) that tantalum–alkyne complexes thus generated react in a one-to-one fashion with carbonyl compounds to yield allylic alcohols in a regio- and stereoselective manner, and (iii) that cyclotrimerization of alkynes to give substituted benzene derivatives is not observed throughout the reaction.

Tantalum(V) chloride was dissolved in a mixed solvent of 1,2-dimethoxyethane (DME) and benzene and reduced with zinc. In order to avoid the hydrometalation of acetylenes with the tantalum complex bearing a Ta–H bond,[5] we chose zinc as the reducing agent. Because of the poor solubility of $TaCl_5$ in benzene, the addition of DME is essential in order to dissolve the salt and to facilitate the reduction with zinc. This low-valent tantalum complex reacted with alkynes smoothly at 25 °C, and no cyclotrimerization leading to substituted benzene derivatives was observed. The complexation of the low-valent tantalum with acetylenes proceeds faster than that of low-valent niobium[3c,9] with acetylenes. For example, the reduction of 6-dodecyne to 6-dodecene was completed in 30 min at 25 °C with the $TaCl_5$–Zn reagent in a mixed solvent of DME and benzene, while it took 5 h with the $NbCl_5$–Zn system[9] under the same conditions. When the tantalum-6-dodecyne complex 1 was quenched with a NaOD–D_2O solution, a vicinal dideuterated olefin 2 was obtained in 75% yield (Scheme I). This result suggests the potential for use of the tantalum–alkyne complex as a vicinal dianion synthon.[3c,10,11]

Scheme I



Treatment of the tantalum-6-dodecyne complex 1 with 3-phenylpropanal at 25 °C for 20 min afforded the allylic alcohol 4 in 96% yield. The results of the preparation of allylic alcohols from alkynes and carbonyl compounds are summarized in Table I.[12,13]

(*E*)-Allylic alcohols were produced exclusively,[15] as expected from the insertion of a carbonyl group into the

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[1] Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422.

[2] (a) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987**, *109*, 2544. (c) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623. (d) Van Wagenen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495.

[3] (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152. (b) *Ibid.* **1987**, *109*, 6551. (c) Hartung, J. B., Jr.; Pedersen, S. F. *Ibid.* **1989**, *111*, 5468. Quite recently, Pedersen's niobium complexes, $NbCl_3$(DME) and $NbCl_4(THF)_2$ were placed on the market from Aldrich Chemical Co. (d) Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989**, *8*, 1566.

[4] (a) LaPointe, R. E.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 3535. (b) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *Ibid.* **1986**, *108*, 6382.

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[8] (a) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (b) Strickler, J. R.; Waxler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.

[9] Submitted for publication. Pedersen's niobium complex $NbCl_3$(DME) is reported to require gentle reflux in THF to generate niobium-alkyne complexes.[3c]

[10] Prof. S. F. Pedersen reported a one-to-one coupling reaction between acetylenes and aldehydes leading to allylic alcohols via $NbCl_3$(DME). In Abstracts of the 194th ACS National Meeting at New Orleans in 1987, Div. of Org. Chem., No. 218, and footnote 13 of ref 3c.

[11] For a review, see: Maercker, A.; Theis, M. *Top. Curr. Chem.* **1987**, *138*, 1.

[12] **Typical Procedure.** Zinc (0.20 g, 3.0 mmol) was added at 25 °C to a pale yellow solution of $TaCl_5$ (0.72 g, 2.0 mmol) in DME–benzene (1:1, 10 mL) under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue with a slightly exothermic process. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME–benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C for 30 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the mixture was stirred at 25 °C for 15 min, 3-phenylpropanal (0.16 g, 1.2 mmol) was added, and the resulting mixture was stirred at 25 °C for 15 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-super Cel and washed well with ethyl acetate (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel (ethyl acetate–hexane, 1:20) gave (*E*)-5-pentyl-1-phenyl-4-decen-3-ol (4) in 96% yield (0.29 g).

[13] Treatment of aldehydes or ketones with the low-valent tantalum gave the McMurry-type 1,2-diols in excellent yields. Cinnamyl alcohol dimerized with loss of the hydroxyl group to afford a mixture of 1,5-dienes in 73% yield.[14]

[14] For reactions with low-valent niobium, see: Sato, M.; Oshima, K. *Chem. Lett.* **1982**, 157.

[15] The stereochemistry was determined by comparison with authentic samples of (*E*)- and/or (*Z*)-allylic alcohols.[16] Geometric purity was ascertained by examination of ^1H or ^{13}C NMR spectra and/or capillary GLPC and is estimated to be >98% in all cases.

[16] (a) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754 and 5085. (b) Sato, F.; Ishikawa, H.; Sato, S. *Tetrahedron Lett.* **1981**, *22*, 85. (d) Ichinose, Y.; Nozaki, K.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 3709.

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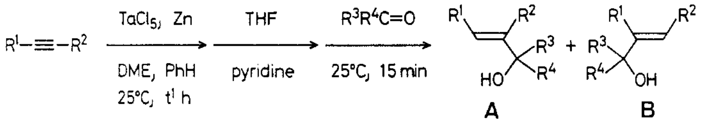
Table I. Synthesis of Allylic Alcohols from Acetylenes and Aldehydes[a]



run	R^1	R^2	R^3	R^4	time t^1, h	yield,[b] %	A/B[c]
1	n-$C_{10}H_{21}$	H	n-C_8H_{17}	H	0.7	48[d]	>99/<1
2			$-(CH_2)_5-$		0.7	45[d]	>99/<1
3	n-C_5H_{11}	n-C_5H_{11}	Ph	H	0.5	85	–
4			n-C_8H_{17}	H	0.5	94	–
5			c-C_6H_{11}	H	0.5	75	–
6			$-(CH_2)_5-$		0.5	87	–
7	c-C_6H_{11}	n-C_6H_{13}	$Ph(CH_2)_2$	H	1.5	80	65/35
8			$-(CH_2)_5-$		1.5	83	76/24
9	t-Bu	n-C_7H_{15} (**6**)	$Ph(CH_2)_2$	H	4.5	67[e,f]	>99/<1
10			$-(CH_2)_5-$		4.5	<5[e,g]	–
11	n-C_6H_{13}	Ph (**7**)	$Ph(CH_2)_2$	H	1	73	83/17
12			$-(CH_2)_5-$		1	80	79/21
13	Me_3Si	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	H	1.5	77[h]	89/11
14			$-(CH_2)_5-$		1.5	85[h]	>99/<1
15	Me_3Si	Ph	$Ph(CH_2)_2$	H	3	71[e]	>99/<1
16	t-$BuMe_2Si$	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	H	3	68[e,h]	>99/<1
17			$-(CH_2)_5-$		3	71[e,h]	>99/<1

[a] For experimental details, see ref 12. [b] Isolated yields. [c] Reference 15. [d] $TaCl_5$ (1.0 equiv), zinc (1.5 equiv), and pyridine (2.0 equiv) were employed. Tantalum–1-dodecyne complex was treated with a carbonyl compound (1.2 equiv) at 25 °C for 45 min. Polymeric products of 1-dodecyne were produced in ca. 40% yield. [e] $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. [f] (*Z*)-2,2-Dimethyl-3-undecene (**8**) was obtained in 24% yield. [g] Recovery of unreacted olefin **8**: 81% yield. Cyclohexanone was recovered in 32% yield and the McMurry-type 1,2-diol of cyclohexanone was produced in 45% yield. [h] The reaction was conducted without addition of pyridine.

tantalum–carbon bonds of the alkyne complexes. The regioselectivity (A/B) of the adduct with the tantalum–alkyne complex is higher than that observed with a zirconocene–alkyne complex.[2b,d] The bulkiness of the substituents R^1, R^2, R^3, and R^4 influences the regiochemistry of the products. Thus, as R^1, R^3, or R^4 become bigger, or as R^2 becomes smaller, higher regioselectivities (A/B) are obtained (except runs 11 and 12). In the case of the sterically crowded acetylene **6**, both reactions, reduction of the acetylenic bond and addition of the tantalum–alkyne complex to carbonyl compounds, were retarded (runs 9 and 10). The results of the reactions between the aromatic acetylene **7** and carbonyl compounds reveal that electronic effects are also directing factors of the regiochemistry (runs 11 and 12). In the case of terminal acetylenes, significant amounts (ca. 40% yield) of polymeric products were obtained as byproducts, but this did not involve cyclotrimerized aromatic compounds (runs 1 and 2).[7,8]

Yields of allylic alcohols depended on additives prior to addition of the aldehyde. The coupling reaction between the tantalum–alkyne complex and an aldehyde without addition of THF was marginal, and many byproducts appeared. Pretreatment with pyridine before addition of carbonyl compounds was essential to suppress the formation of 1,3-dienes through dehydration of an allylic alcohol, especially in the case of a ketone.

As shown in Scheme I, the intermediate **3** could be trapped with D_2O and I_2 to give deuterated alcohol **4-*d*** and iodo alcohol **5** in 68% and 76% yields, respectively.

The scope and limitations of this low-valent tantalum complex and the use of the tantalum-containing intermediates **1** and **3** are currently under investigation.

Acknowledgment. We thank the Ministry of Education, Science, and Culture of Japan for financial support.