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REDUCTION OF ACETYLENES TO (Z)-OLEFINS BY MEANS OF LOW-VALENT NIOBIUM OR TANTALUM.

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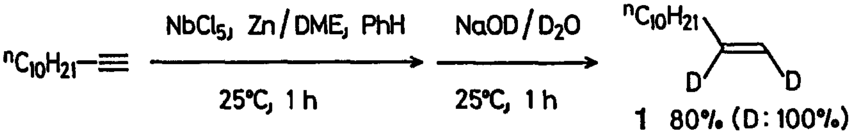
Summary: Partial reduction of alkynes to (Z)-alkenes is achieved with the low-valent group 5 metal reagents prepared from $MtlCl_5$ (Mtl = Nb or Ta) and zinc in a mixed solvent of DME (or THF) and benzene.

In 1982, we reported low-valent niobium prepared by the reduction of $NbCl_5$ with $NaAlH_4$ and used it for some reductions, i.e. the McMurry type reductive coupling of aldehydes or ketones and reduction of acetylenes.[1] In the latter reaction with internal acetylenes, higher Z preference in produced olefins was recognized compared to $TiCl_4$-$LiAlH_4$ reagent.[2] This observation suggests the formation of a niobium-alkyne complex[3-5] as an intermediate or existence of a hydrometalation step by Nb-H species.[6] However, quenching of the reaction mixture of an internal acetylene with D_2O did not give a deuterated olefin. Thus, we reexamined our previous niobium chemistry under the condition using a reducing agent having no hydride source. In contrast to the previous $NbCl_5$-$NaAlH_4$ system,[1] a combination of $NbCl_5$ and zinc was found to give a vicinal dideuterated olefin after being quenched the reaction mixture with NaOD-D_2O. For example, treatment of 1-dodecyne with the combination of 4 equiv of $NbCl_5$ and 6 equiv of zinc in DME-benzene (1:1) afforded 1,2-dideuterio-1-dodecene (1) in 80% yield (Eq. 1).



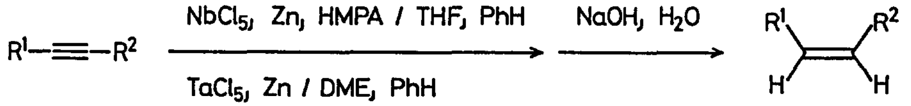
1 80% (D: 100%)

(1)

Results of the reduction with the $NbCl_5$-Zn system are summarized in the upper part of Table 1. Reduction of internal acetylenes with the niobium system gave (Z)-olefins exclusively except silyl acetylene **3** where partial isomerization took place during the reduction (run 8).

The rate of reduction of acetylenes varies with the solvent system and the bulkiness of the substituents of the acetylenes. For example, treatment of internal acetylene, 6-dodecyne, with 2 equiv of the $NbCl_5$-Zn reagent in DME-benzene (1:1) at 25°C for 18 h gave 6-dodecene in 52% yield along with 18% of the starting acetylene.[7] Meanwhile, 74% of 6-dodecene was obtained when the reduction was conducted in a mixed solvent of THF-benzene (1:2) and HMPA (double molar quantity of $NbCl_5$).[8] Acetylenes **2** and **3** having bulky

Table 1. Reduction of acetylenes to (Z)-olefins by means of the low-valent niobium or tantalum.



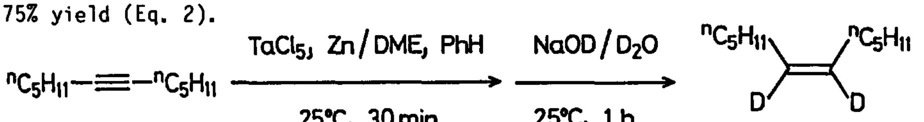
Run	R^1	R^2	Method[a]	Time/h	Yield/%[b]	Z/E[c]
1	$^{n}C_{10}H_{21}$-	H	Nb	1	72[d]	--
2	Ph	H		2	81[d,e]	--
3	$^{n}C_5H_{11}$-	$^{n}C_5H_{11}$-		20	74	>99/<1
4	-$(CH_2)_{10}$-			7	82	>99/<1[f]
5	Ph	$^{n}C_6H_{13}$-		20	86[g]	>99/<1
6	$^{c}C_6H_{11}$-	$^{n}C_6H_{13}$-		40	81[g]	97/3
7	^{t}Bu	$^{n}C_7H_{15}$- (2)		40	62[g]	89/11
8	Me_3Si-	$^{n}C_{10}H_{21}$- (3)		40	81[g]	93/7[f]
9	$^{n}C_{10}H_{21}$-	H	Ta	2	52[h,i]	--
10	Ph	H		1	68[e]	--
11	$^{n}C_5H_{11}$-	$^{n}C_5H_{11}$-		0.5	85	>99/<1
12	-$(CH_2)_{10}$-			0.3	69	>99/<1[f]
13	Ph	$^{n}C_6H_{13}$-		0.5	85	>99/<1
14	$^{c}C_6H_{11}$-	$^{n}C_6H_{13}$-		4	80	>99/<1
15	^{t}Bu	$^{n}C_7H_{15}$- (2)		4.5	82[j]	>99/<1
16	Me_3Si-	$^{n}C_{10}H_{21}$- (3)		2	79	89/11[f]
17	^{n}Bu	$CH_2{=}CH(CH_2)_3$-		0.6	81[k]	>99/<1
18	$^{n}C_{10}H_{21}$-	$CH_2{=}CH(CH_2)_4$-		0.6	82[k]	>99/<1

a) Nb: The acetylene (1.0 mmol) was treated at 25°C with a reagent prepared from $NbCl_5$ (2.0 mmol), Zn (6.0 mmol), and HMPA (4.0 mmol) in THF-benzene (1:2). Ta: The acetylene (1.0 mmol) was treated at 25°C with a reagent prepared from $TaCl_5$ (2.0 mmol), Zn (3.0 mmol) in DME-benzene (1:1). b) Isolated yields unless otherwise noted. c) The Z/E ratios were determined by capillary GLPC analysis of the corresponding epoxides unless otherwise noted. d) The reduction was conducted at 0°C in DME-benzene (1:1). Four-fold excess of low-valent niobium ($NbCl_5$ (4.0 mmol) and Zn (6.0 mmol)) were employed, as undesirable dimerization of the acetylene took place when unreacted acetylene remained. e) GLPC yield. f) The Z/E ratios were determined by capillary GLPC and/or ^{1}H NMR analysis of the product olefins. g) Mixed solvent of THF-benzene-HMPA (1:2:1) was employed to accelerate the reduction. h) One equiv of $TaCl_5$ and 1.5 equiv of zinc were employed. Two equiv of TMEDA was added before addition of 1-dodecyne. i) Dodecane was produced in 2% yield. j) Four equiv of $TaCl_5$ and 6 equiv of zinc were used, as the acetylene remained with the standard amounts of the reagent. k) Internal olefin was produced in about 5% through overreduction of a terminal double bond.

substituents like t-butyl and silyl groups are marginal even by addition of 4 equiv of HMPA. Thus the amount of HMPA was increased to 25 vol% of the mixed solvent of THF-benzene-HMPA. In contrast, terminal acetylenes are too reactive to undergo undesirable overreduction with the low-valent niobium in the THF-benzene-HMPA system. Thus the reaction was conducted in DME-benzene (1:1).[9]

Aluminium powder can be employed instead of zinc dust. Ultrasonic irradiation to a mixture of $NbCl_5$ and aluminium in DME-benzene (1:1) before addition of alkynes is indispensable to get reproducible results.[10] Meanwhile, reduction of acetylenes with a reagent derived from $NbCl_5$ and magnesium gave a complex mixture containing the desired olefin and polymeric products.

Low-valent tantalum has been produced from $TaCl_5$ and zinc by analogous method of the niobium. Reduction of acetylenes with the $TaCl_5$-Zn system is summarized in the lower part of the Table 1. Reduction of internal acetylenes with the tantalum system proceeds faster compared to that with the low-valent niobium.[11] Production of isomerized (E)-olefins was suppressed by using the low-valent tantalum except in the case of a silyl acetylene (runs 6,7,14, and 15). Quenching the reaction mixture of the reduction of 6-dodecyne with the low-valent tantalum by the addition of NaOD-D_2O gave also a vicinal dideuterated olefin **4** in 75% yield (Eq. 2).



4 75% (D:100%) (2)

Olefinic double bonds which are capable to participate in cyclization remained intact (runs 17 and 18). This observation shows a sharp contrast to the reaction with low-valent zirconium.[12]

Low-valent group 5 metals react with alkynes to form metal-alkyne complexes.[3-5,13] Introduction of deuterium at cis-vicinal position of alkenes suggests the metal-alkyne complex as an intermediate.[14] Since low-valent group 5 metal complexes such as $CpNbCl_4$-Mg,[5] $Ta(DIPP)_2Cl_3$-Na/Hg,[13c,d] and $Ta_2Cl_6(SC_4H_8)_3$[13a] are reported to catalyze cyclotrimerization of acetylenes, it is of considerable interest that no cyclotrimerization product, i.e. a benzene derivative, was observed throughout the reaction.

Typical Procedure

$NbCl_5$-Zn system: To a stirring pale orange solution of $NbCl_5$ (0.54 g, 2.0 mmol) in THF-benzene (1:2, 15 mL) was added HMPA (0.70 mL, 4.0 mmol) and zinc (0.39 g, 6.0 mmol) successively under an argon atmosphere and the mixture was stirred at 25°C for 40 min. The color of the mixture turned from purple to dark blue with exothermic process. To the mixture was added at 25°C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in THF-benzene (1:2, 1.5 mL) and the whole mixture was stirred at 25°C for 20 h. Aqueous NaOH solution (15%, 2 mL) was added and the mixture was stirred at 25°C for additional 1 h. The precipitated white solid was removed by filtration with Hyflo-super Cel^R and washed with ethyl acetate (3x5 mL). The filtrate and washings were dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel with hexane as an eluent gave 6-dodecene in 74% yield (0.12 g).

$TaCl_5$–Zn system:[15] To a stirring pale yellow solution of $TaCl_5$ (0.72 g, 2.0 mmol) in DME-benzene (1:1, 10 mL) was added zinc (0.20 g, 3.0 mmol) at 25°C 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 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. After being stirred for 30 min, aqueous NaOH solution (15%, 2mL) was added and the mixture was stirred at 25°C for additional 1 h. The deposited white solid was removed by filtration with Hyflo-super Cel^R and washed with ethyl acetate (3x5 mL). The crude product was dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel with hexane as an eluent gave 6-dodecene in 85% yield (0.14 g).

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(7) When 4 equiv of $NbCl_5$ was employed, the reduction of 6-dodecyne was completed in 5.5 h (80% yield).
(8) When the reduction was conducted in a mixed solvent of THF-benzene-HMPA, introduction of deuteriums at vicinal olefinic positions of 6-dodecene with NaOD-D_2O was only 45%. Thus the mixed solvent of THF-benzene-HMPA was not employed in the following coupling reaction with o-phthalaldehyde.
(9) Reduction of terminal acetylenes with the $NbCl_5$-$NaAlH_4$ system gives a complex mixture. See ref. 1
(10) A mixture of $NbCl_5$ (4.0 equiv) and aluminium metal (6.0 equiv) in DME-benzene after ultrasonic irradiation shows dark orange color. Reduction of 1-dodecyne with the $NbCl_5$-Al reagent at 25°C for 1.5 h in DME-benzene (1:1) afforded 1-dodecene in 89% yield.
(11) Complexation of $NbCl_3$(DME) with alkynes is reported to require gentle reflux of THF for 10–14 h. See ref 4.
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(14) The other reactions which suggest the metal-alkyne intermediate are shown in the following paper.
(15) Aldehydes and ketones were converted into the McMurry-type 1,2-diols with the low-valent tantalum (or niobium). For example, treatment of 3-phenylpropanal and cyclohexanone with the $TaCl_5$-Zn reagent in DME-benzene at 25°C for 10 min afforded the corresponding 1,2-diols in 99% and 82% yields, respectively. Cinnamyl alcohol dimerized with loss of the hydroxyl group to afford a mixture of 1,5-dienes in 73% yield by the action of the low-valent tantalum. See also ref. 1.

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