

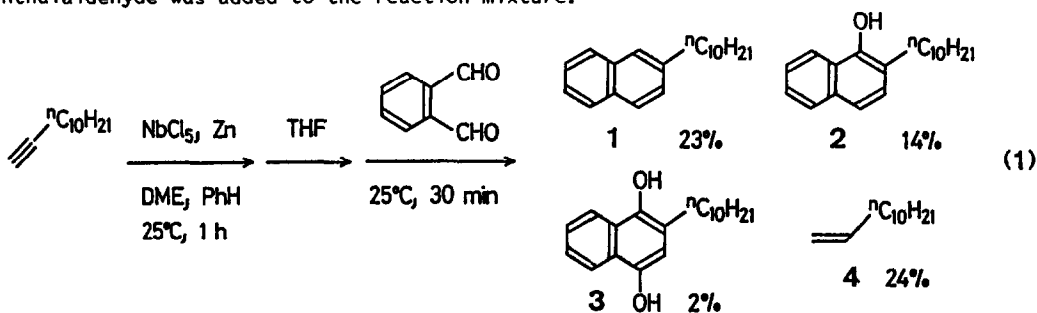
PREPARATION OF 1-NAPHTHOLS FROM ACETYLENES AND *o*-PHTHALALDEHYDE
USING LOW-VALENT TANTALUM AND NIOBIUM.

Yasutaka Kataoka, Jiro Miyai, Makoto Tezuka, Kazuhiko Takai,*
Koichiro Oshima, and Kiitiro Utimoto*
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606, Japan

Summary: Tantalum (or niobium)-alkyne complexes are produced by treatment of acetylenes with the low-valent tantalum (niobium) derived by zinc reduction of TaCl₅ (NbCl₅). Substituted 1-naphthols are prepared regioselectively by reaction of *o*-phthalaldehyde with the tantalum (or niobium)-alkyne complexes in good to excellent yields.

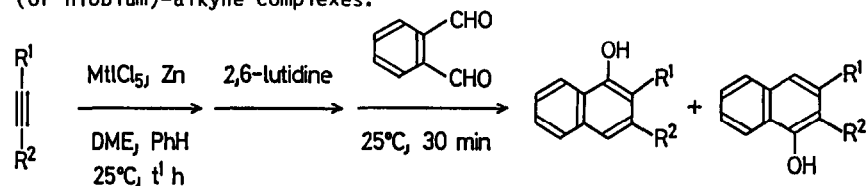
Recent report by Pedersen¹ about the preparation of 1-naphthol derivatives with NbCl₃(DME) prompted us to report our independent work on preparation of 1-naphthols with low-valent group 5 metals derived by reduction of TaCl₅ (or NbCl₅) with zinc.

We have already shown that unisolable niobium-alkyne complexes^{1,2} can be produced by reaction of alkynes with the low-valent niobium derived from NbCl₅ and zinc.³ Tantalum-alkyne complexes⁴ have also been produced *in situ* from acetylenes and a combination of TaCl₅ and zinc by the analogous method of the low-valent niobium.³ To examine the use of the metal-alkyne complexes as a vicinal dianion synthon,^{1,5} *o*-phthalaldehyde was added to the reaction mixture.



Treatment of a niobium-1-dodecyne complex with *o*-phthalaldehyde (2 equiv) in DME-benzene-THF at 25°C gave a mixture of three compounds having naphthalene skeleton 1, 2, 3, and 1-dodecene (4) in 23%, 14%, 2%, and 24% yields, as shown in Eq. 1. Several additives were examined to obtain one of the naphthalene compounds in a selective manner. An addition of amines increased the production of 2-decyl-1-naphthol (2) and decreased the yield of that of 2-decyl-naphthalene (1). Among those amines examined, 2,6-lutidine gave the best result.⁶ In contrast to the terminal acetylenes, internal acetylenes afforded only 2,3-disubstituted-1-naphthol derivatives without any additives.

Table 1. Preparation of 1-naphthols by the reaction of *o*-phthalaldehyde with tantalum (or niobium)-alkyne complexes.



Run	R ¹	R ²	Mt ^{1a}	Time t ¹ /h	Aldehyde equiv	Product ^b ratio	Yield %
1	ⁿ C ₅ H ₁₁ -	ⁿ C ₅ H ₁₁ -	Ta	0.5	2		84
2			Nb	10	2		93
3	Ph	Ph	Ta	6 ^c	3		70
4	-(CH ₂) ₁₀ -		Ta	0.5	4		70 ^{d, e}
5	ⁿ C ₆ H ₁₃ -	^c C ₆ H ₁₁ - (5)	Ta	2	3		>98: <2
6			Nb	11	3		67: 33
7	ⁿ C ₇ H ₁₅ -	^t Bu	Ta	4.5	3		71 ^{f, h}
8	Me	Ph	Ta	0.5	3		71:29 ⁱ
9	ⁿ C ₆ H ₁₃ -	Ph	Ta	2	3		75:25
10			Nb	12	3		55:45
11	ⁿ C ₁₀ H ₂₁ -	H	Nb	1	3		59 ^f
12	Ph	H	Nb	2	3		31 ^f
13	ⁿ C ₁₀ H ₂₁ -	Me ₃ Si	Ta	1.5	3		88 ^{f, j}
14	Ph	Me ₃ Si	Ta	7	3		64 ^{f, j}

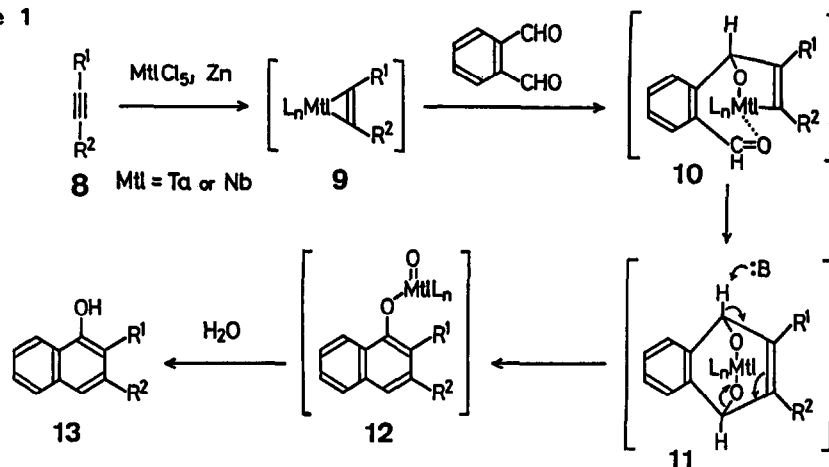
a) Ta: A tantalum-alkyne complex, prepared by treatment of an acetylene (1.0 mmol) with a low-valent tantalum derived from TaCl₅ (2.0 mmol) and zinc (3.0 mmol), was treated with 2,6-lutidine (4.0 mmol) and *o*-phthalaldehyde (3.0 mmol). Nb: Low-valent niobium was generated upon treatment of NbCl₅ (4.0 mmol) with zinc (6.0 mmol) and employed instead of the low-valent tantalum. b) Isolated yields. c) Complexation of diphenylacetylene with the low-valent tantalum was conducted at 50°C. d) HMPA (2.0 mmol) was used instead of 2,6-lutidine. e) Cyclododecene was obtained in 21% yield. f) The other regioisomer was not observed. g) Reaction of 5 with the Pedersen's niobium complex NbCl₃(DME) produced the same regioisomer 6 as a main product (6/7=86/14) in our hands. h) Four mmol of TaCl₅ and 6.0 mmol of zinc were employed. i) See ref. 10. j) Regiochemistry was ascertained by desilylation with CF₃CO₂H (ref. 9).

However, pretreatment of the niobium-alkyne complex with 2,6-lutidine also gave the best yields. Tantalum-alkyne complexes, which was formed smoothly compared to the niobium complexes,³ reacted with *o*-phthalaldehyde to afford 1-naphthol derivatives.⁷ Preparation of 1-naphthols from acetylenes and *o*-phthalaldehyde is summarized in Table 1.

Reactions between terminal acetylenes and *o*-phthalaldehyde gave 2-substituted-1-naphthols regioselectively⁸ and 3-substituted ones were not observed (runs 11 and 12). There is a tendency that bulky substituents occupy 3-position of the 2,3-disubstituted-1-naphthols in the case of unsymmetrically disubstituted acetylenes especially when tantalum-alkyne complexes were employed (runs 5,6, and 8-10). One of the regioisomers was produced exclusively when the bulkiness of the substituent differs greatly from the other (runs 7, 13 and 14).

Formation of 1-naphthol 13 can be explained as follows (Scheme 1). Low-valent tantalum (or niobium), generated from TaCl₅ (NbCl₅) and zinc, reacts with an alkyne 8 to produce a metal-alkyne complex 9. Insertion of a formyl group into a metal-carbon bond of the complex 9 gives 10. Internal coordination of the second formyl group at the suitable position of 10 facilitates the second insertion reaction leading to 11. Elimination of a metaloxy group at benzylic position of 11 takes place to generate 12, which affords 1-naphthol 13 after aqueous workup. Strong affinity of Mtl-O bond (Mtl = Ta or Nb)¹¹ and aromatic stabilization can be the driving force of the elimination.

Scheme 1



Since substitution reactions of trimethylsilyl (Me₃Si-),¹² diethoxyphosphoryloxy ((EtO)₂P(O)O-),¹³ and trifluoromethanesulfonyloxy (TfO-) groups¹⁴ attached on aromatic rings are known to proceed smoothly under palladium or nickel catalysis, this method provides new access of substituted naphthalene derivatives.

Typical Procedure with TaCl₅-Zn: To a stirring pale yellow solution of TaCl₅ (0.72 g, 2.0 mmol) in DME-benzene (1:1, 20 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 for 30 min. 2,6-Lutidine (0.47 mL, 4.0 mmol) was added to the mixture. After being stirred at 25°C for 20 min, a solution of o-phthalaldehyde (0.40 g, 3.0 mmol) in DME-benzene (1:1, 2 mL) was added to the mixture and the resulting mixture was stirred at 25°C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added and the mixture was stirred at 25°C for additional 1 h. The deposited solid was removed by filtration with Hyflo-super Cel^R and washed with ethyl acetate (3x5 mL). The filtrate and washings were concentrated. Resulting viscous solid was extracted well with hexane (5x5 mL) and the extracts were dried over Na₂SO₄ and concentrated again. Purification by column chromatography on silica gel (ethyl acetate-hexane, 1:10) gave 2,3-dipentyl-1-naphthol in 85% yield (0.24 g). Preparation of 1-naphthols with low-valent niobium is almost the same as the tantalum case except the formation of niobium-alkyne complexes. See the preceding paper.³

References and Notes

- (1) J. B. Hartung, Jr., and S. F. Pedersen, J. Am. Chem. Soc., **111**, 5468 (1989).
- (2) (a) S. Fredericks and J. L. Thomas, J. Am. Chem. Soc., **100**, 350 (1978). (b) A. C. Williams, P. Sheffels, D. Sheehan, and T. Livinghouse, Organometallics, **8**, 1566 (1989).
- (3) Y. Kataoka, K. Takai, K. Oshima, and K. Utimoto, Tetrahedron Lett., preceding paper in this issue. The structure of the niobium and tantalum-alkyne complexes was not confirmed spectroscopically.
- (4) (a) J. A. Labinger, J. Schwartz, and J. M. Townsend, J. Am. Chem. Soc., **96**, 4009 (1974). (b) F. A. Cotton and W. T. Hall, Inorg. Chem., **19**, 2352 (1980). (c) M. D. Curtis and J. Real, J. Am. Chem. Soc., **108**, 4668 (1986). (d) J. R. Strickler, P. A. Wexler, and D. Wigley, Organometallics, **7**, 2067 (1988).
- (5) For a review, see: A. Maercker and M. Theis, Top. Curr. Chem., **138**, 1 (1987).
- (6) Additives and the yields (%) of the four compounds 1, 2, 3, and 4 are as follows (conditions: 1-dodecyne (1.0), o-phthalaldehyde (2.0), NbCl₅ (4.0), Zn (6.0), DME-benzene-THF (1:1:1), 25°C, 30 min): HMPA (4.0), 8, 50, 11, 27; TMEDA (4.0), 2, 45, 5, 22; Et₃N (4.0), 4, 45, 7, 11; pyridine (8.0), 0, 45, 7, 7; 2,6-lutidine (8.0), 0, 53, 5, 22; 2,6-lutidine (8.0)-o-phthalaldehyde (3.0), 0, 59, 4, 14.
- (7) Tantalum-alkyne complexes add to carbonyl compounds in a one to one fashion to afford (E)-allylic alcohols stereoselectively. Submitted for publication.
- (8) M. Watanabe, S. Hisamatsu, H. Hotokezaka, and S. Furukawa, Chem. Pharm. Bull., **34**, 2810 (1986).
- (9) R. L. Funk and K. P. C. Vollhardt, J. Am. Chem. Soc., **1980**, **102**, 5253.
- (10) The authentic samples were prepared according to the following reference. M. F. Semmelhack, S. Ho, M. Steigerwald, and M. C. Lee, J. Am. Chem. Soc., **109**, 4397 (1987).
- (11) J. A. Kerr and A. F. Trotman-Dickenson, "Strength of Chemical Bonds," in CRC Handbook of Chemistry and Physics, CRC Press Inc., Cleveland.
- (12) For the wide use of aryltrimethylsilanes in synthesis, see: (a) E. Colvin, "Silicon in Organic Synthesis," Butterworths, London, 1981, p.125. (b) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer, Berlin, 1983, p. 114.
- (13) T. Hayashi, Y. Katsuro, Y. Okamoto, and M. Kumada, Tetrahedron Lett., **22**, 4449 (1981).
- (14) S. Cacchi, P. G. Ciattini, E. Morera, and G. Ortar, Tetrahedron Lett., **27**, 3931, 5541 (1986).

(Received in Japan 25 September 1989)