CHEMISTRY LETTERS, pp. 1721-1724, 1988.

A Convenient Method for Dihydroxylation of Olefins by the Combined Use of Osmium Tetroxide and Dihydroxyphenylborane

Nobuharu IWASAWA, Takashi KATO, and Koichi NARASAKA
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

cis-Dihydroxylation of olefins with a catalytic amount of osmium tetroxide and N-methylmorpholine N-oxide proceeds smoothly in an organic solvent by the use of dihydroxyphenylborane, giving the corresponding 2-phenyl-1,3,2-dioxaborolane derivatives (phenylboronic esters) in good yields.

Dihydroxylation of olefins by osmium tetroxide is one of the most efficient method for the introduction of vicinal cis-dihydroxy functionalities to the carbon-carbon double bond,$^{1)}$ and is frequently employed in the total synthesis of highly-oxygenated natural products. However, due to its high cost and toxicity, catalytic use of osmium tetroxide has been required, and a variety of co-oxidants have been employed for this purpose.$^{2)}$ For example, N-methylmorpholine N-oxide is known to be a very mild and efficient co-oxidant and is commonly used in synthetic procedures.$^{3)}$ These catalytic procedures, however, sometimes accompany further oxidation of the generated 1,2-cis-diols. And an aqueous solvent is usually employed to hydrolyze the osmium ester, which makes it difficult to isolate water soluble polyol derivatives. To avoid such difficulties, it was assumed that the addition of some trapping reagent of diols could prevent further oxidation of the products and also make the isolation procedure easier.

Now, we wish to report a facile method for dihydroxylation of olefins in an organic solvent by the use of dihydroxyphenylborane as a diol captor.$^{4)}$

In the first place, we examined various diol captors taking dihydroxylation of indene as a model reaction. That is, to a dichloromethane solution of 2 mol% amount of osmium tetroxide, N-methylmorpholine N-oxide, a diol captor and indene were added successively at room temperature. Work-up of the mixture gave the corresponding cis-diol or its derivatives. As shown in the Table 1, dihydroxyborane derivatives were found to be effective as diol captors. Especially, using dihydroxyphenylborane, 2-phenyl-1,3,2-dioxaborolane derivative (phenylboronic ester, **1a**) was obtained in high yield. When the reaction was carried out in an aqueous solution in the absence of dihydroxyphenylborane (5 mol% of osmium tetroxide, 1.1 mol amount of N-methylmorpholine N-oxide, in acetone-water(5:1)), the cis-diol (**1c**) was obtained in 68% yield after 1 d along with side products. Thus, it is apparent that the formation of phenylboronic ester during the reaction effectively prevents further oxidation of the dihydroxylated

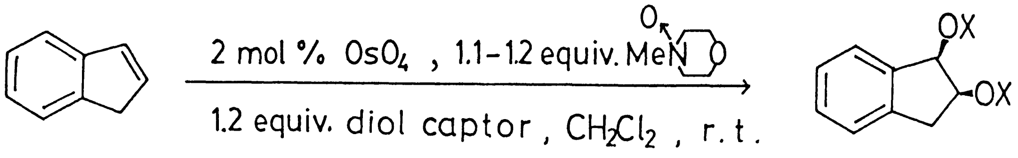
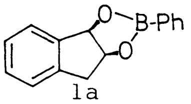
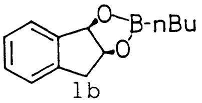
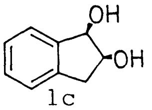


Table 1. The Examination of the Diol Captor

Captor	Reaction time	Product	Yield/%
$PhB(OH)_2$	15 min	 1a	93
$n\text{-}BuB(OH)_2$	1 h	 1b	83
$B(OH)_3$	4 h	 1c	67
$Ph_2Si(OH)_2$	2 d	1c	41
Ph_2SnO	12 h	1c	75

product.

Next, we examined this reaction using various alkenes. As shown in Table 2, the desired phenylboronic esters are obtained in high yield. In the case of the oxidation of dienes such as cyclooctadiene and norbornadiene, the corresponding phenylboronic esters were obtained in good yield even by using exess amounts of N-methylmorpholine N-oxide. On the other hand, application of the conventional methods to the oxidation of dienes does not always give good results$^{3)}$ probably due to the over-oxidation of the products and the difficulty in extracting the tetraols from aqueous medium. This reaction, therefore, gives a satisfactory solution to these problems.

Typical experimental procedure is as follows: To a dichloromethane solution (1 ml) of osmium tetroxide (5 mg), N-methylmorpholine N-oxide (140 mg, 1.19 mmol), and dihydroxyphenylborane (143 mg, 1.17 mmol) was added a dichloromethane solution (2 ml) of indene (107 mg, 0.92 mmol) at room temperature. After stirring 15 minutes at that temperature, 10% $NaHSO_3$ solution (5 ml) was added and the mixture was stirred for 1 h to decompose osmium tetroxide. Organic materials were extracted with ethyl acetate, and the combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (silica gel) to afford the corresponding phenylboronic ester (202 mg, 0.86 mmol, 93% yield).

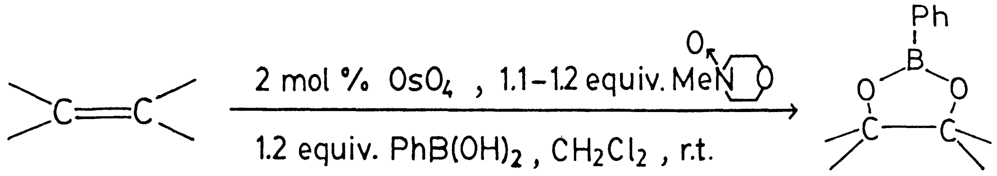
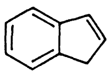
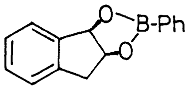
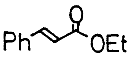
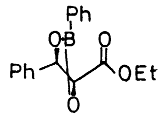
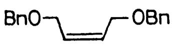
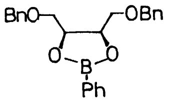
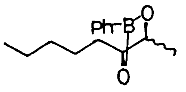
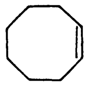
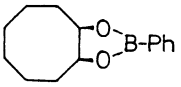
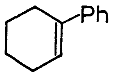
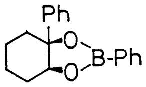
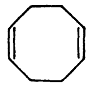
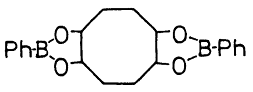
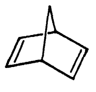
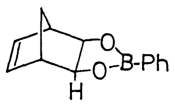
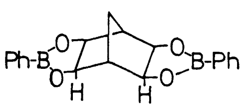


Table 2. Synthesis of Phenylboronic Esters from Olefins

Olefin	Reaction time	Product	Yield/%
	15 min		93
	12 h		92
	2 h		86
 a)	30 min		86
	20 h		87
	4 h		93
 b)	30 min	 c)	81
 b)	12 h	 d)	60
			12

a) Mixture of (Z)- and (E)-isomers.

b) 3.0 molar amounts of N-methylmorpholine N-oxide and dihydroxyphenylborane were used.

c) Ca. 1:1 mixture of cis and trans isomers.

d) Only exo isomer was obtained.

The stereochemistry of this reaction was examined by the oxidation of (Z)- and (E)-2-pentenes. Authentic samples were prepared by the reaction of dihydroxyphenylborane and 2,3-pentanediols which were prepared by the known cis-dihydroxylation[5] of (Z)- and (E)-2-pentenes. And the phenylboronic esters obtained from (Z)- and (E)-2-pentenes by the present method were identical with the authentic samples prepared from (Z)- and (E)-2-pentenes, respectively. That is, cis-dihydroxylation reaction also proceeded specifically to carbon-carbon double bond in the presence of dihydroxyphenylborane.

Furthermore, the reaction in the presence of dihydroxyphenylborane proceeds faster than the reactions which are carried out in dichloromethane containing a small amount of water or in aqueous acetone. For example, by employing dihydroxyphenylborane the phenylboronic ester (**1a**) was produced in 80% yield after 10 min. On the other hand, in the presence of water instead of dihydroxyphenylborane, the diol (**1c**) was produced only in 35% yield after the same reaction time (ca. 10% in aqueous acetone). These results indicate that dihydroxyphenylborane might participate in the dissociation of the osmium ester to facilitate the cleavage of the ester linkages.

The present method of osmium tetroxide oxidation by the combined use of dihydroxyphenylborane in an organic solvent would be useful for the oxidation of olefinic substrates which give the unstable diols or water soluble polyhydroxy compounds.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 63740279 from the Ministry of Education, Science and Culture.

References

1) M. Schroder, Chem. Rev., 80, 187 (1980); H. S. Singh, "Organic Syntheses by Oxidation with Metal Compounds," ed by W. J. Mijs and R. H. I. de Jong, Plenum Press, New York (1986), Chap. 12.
2) N. A. Milas, S. Sussaman, and H. S. Mason, J. Am. Chem. Soc., 61, 1844 (1939); K. Akashi, R. E. Palermo, and K. B. Sharpless, J. Org. Chem. 43, 2063 (1978); G. Braun, J. Am. Chem. Soc., 51, 228 (1929); W. D. Lloyede, B. J. Navarette, and M. F. Shaw, Synthesis, 1972, 610.
3) V. Van. Pheenen, R. C. Kelly, and D. Y. Cha, Tetrahedron Lett., 23, 1973 (1976).
4) T. W. Greene, "Protective Groups in Organic Synthesis," John Wiley & Sons, New York (1981), Chap. 2, p. 85.
5) cis-Dihydroxylation was carried out according to the procedure described in Ref. 3.

(Received July 26, 1988)