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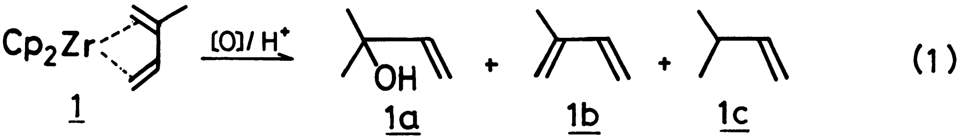
REGIOSELECTIVE OXIDATION OF ZIRCONIUM-DIENE AND ALLYLIC ZIRCONIUM COMPLEXES LEADING TO ALLYLIC ALCOHOLS

Hajime YASUDA, Kinya NAGASUNA, Keiichi ASAMI, and Akira NAKAMURA*
Department of Macromolecular Science, Faculty of Science,
Osaka University, Toyonaka, Osaka 560

Oxidation of zirconium-isoprene or α-myrcene complex with aq. H_2O_2 gave 2-methyl-3-buten-2-ol or linalool, respectively, in good yield. A series of allylic zirconium complexes afforded allylic alcohols, and oxazirconacyclic complexes gave diols by oxidation with H_2O_2, t-BuOOH, MCPBA or oxygen. Iodination of these complexes was also examined.

In the preceding paper we have reported the preparation of a series of $Zr(C_5H_5)_2$(diene)[1)] which reacts regioselectively with alkenes and alkynes to give allylic zirconium complexes.[2)] The reaction with carbonyl compounds gave oxametallacycles.[3)]

We wish to report herein the regioselective oxidation of these complexes with various oxidizing agents. The conversion of Zr-C bonds to Zr-O-C bonds by controlled oxidation is valuable for organic synthesis. However, such a reaction has rarely been reported for early transition metal complexes[4a)] except for the communi-



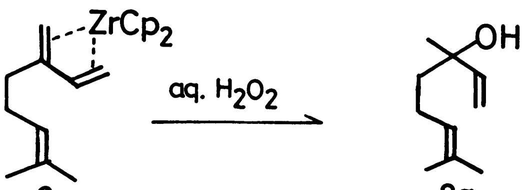
(1)

Table 1. Distribution of the product obtained by oxidation of Cp_2Zr(isoprene) 1

Oxidizing agents	1a	1b	1c	Total yield/%
H_2O_2(30% aq. soln.)	62	29	9	97
t-BuOOH	38	52	10	95
MCPBA	7	84	9	99
O_2/H^+	0	100	0	99

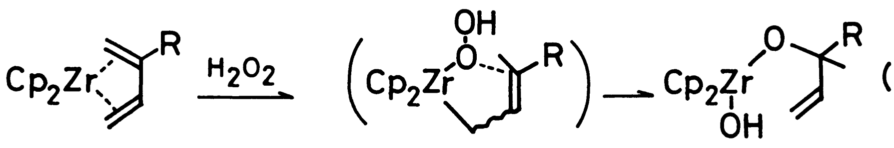
cation by Schwartz on the oxidation of $Cp_2ZrCl(R)$ to give alkyl alcohol.[4b)] This paper deals with the oxidation of organometallic zirconium complexes involving η^4-diene, η^3- or η^1-allyl or η^1-pentadienyl ligand and of oxametallacycles to lead to a variety of unsaturated alcohols. Oxidizing agents used in this work are aqueous hydrogen peroxide(30% H_2O_2), t-butyl hydroperoxide(t-BuOOH), m-chloroperoxibenzoic acid(MCPBA) and O_2.

The result of the oxidation of $Cp_2Zr(\eta^4$-isoprene) 1 in ether at 0°C is listed in Table 1. The use of H_2O_2 is found best to obtain the allylic alcohol,1a. Oxygen or dry air must be avoided for this purpose because it immediately releases isoprene (1b) quantitatively at 0-30°C. Characteristics of the reaction with H_2O_2 lie in 1) predominance of oxidation over hydrolysis in aqueous solution and 2) regioselective oxidation at the C_2 atom of the coordinated isoprene. The oxidation of $Zr(C_5H_5)_2(\eta^4$-myrcene)[5)] also gave the similar result (eq. 2); i.e., (±)-linalool 2a was obtained in 66 % yield together with myrcene(26 %) when aq. H_2O_2 was added to the complex at -20°C and the solution was allowed to warm to room temperature. The C_3-atom of myrcene(which corresponds to the C_2 atom of isoprene) was oxidized regioselectively (99 %). Raising the reaction temperature resulted in the modest change in the yield(58 %). It is noteworthy that the oxidation of myrcenylborane occurred at the terminal C_1 atom[6)] while that of Zr-myrcene complex occurred at the C_3 atom. The proposed mechanism (eq. 3) for this oxidation involves a protonation sequence giving an allylic zirconium complex which was then isomerized to allyloxymetal species by oxidation. The regioselection is due to the inductive effect of alkyl group which increases the negative charge on the C_1 atom.



2 2a

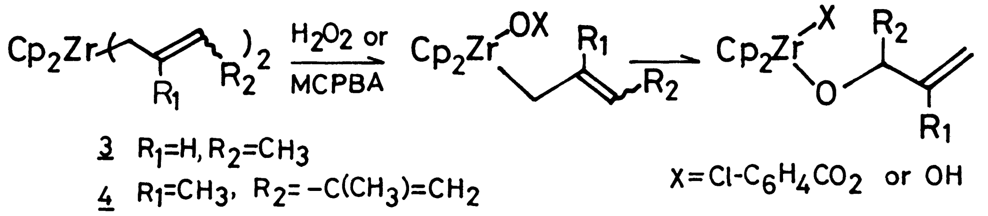
Yield: 66%(-20°C) 58%(30°C) (2)



(3)

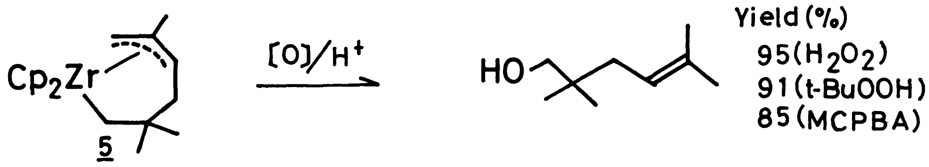
R= CH_3, $-(CH_2)_2CH=C(CH_3)_2$

Above results prompted us to examine the oxidation of η^1-allylic zirconium complexes to allyl alcohols. $Cp_2Zr(2\text{-butenyl})_2$ 3 prepared from Cp_2ZrCl_2 and C_4H_7MgCl gave 1-buten-3-ol in 42 % yield by reaction with H_2O_2 at 0°C in ether, accompanied by a hydrolysis product, 1-butene(58 %). One of the butenyl groups may be cleaved preferentially by protonation to give $Cp_2Zr(OOH)$(2-butenyl) and then the oxidation occurs at the remaining butenyl zirconium part; i.e., oxidation becomes feasible when the charge density on metal decreases. Bis(pentadienyl)-zirconium complexes also showed the similar behavior; i.e., oxidation of Cp_2Zr-(2,4-dimethyl-2,4-pentadienyl)$_2$$^{7)}$ with MCPBA gave 2,4-dimethyl-1,4-pentadien-3-ol (48 %), 2,4-diemthyl-1,3-pentadiene(38 %) and 2,4-dimethyl-1,4-pentadiene(12 %).



(4)

A metallacyclic complex (5)$^{8)}$ prepared from Cp_2Zr(isoprene) and 1-olefin, is expected to give an unsaturated alcohol. Actually, oxidation at the σ bonded alkyl metal site and protonation at the other end (allylic metal moiety) occurred selectively (eq. 5). Similar trend was observed in the oxidation of Cp_2M(butadiene dimer) complex (M; Zr, Hf) which has a metallanona-3,7-diene structure in solution. A 25/53 mixture of 1,7-octadien-3-ol and 1,6-octadien-3-ol was obtained in ca. 80 % combined yield for the Zr complex (6a) and a 45/12 mixture for the Hf complex(6b).$^{9)}$ Similarly, Cp_2Zr(isoprene dimer) complex (6c) gave a 21/55 mixture of 2,7-dimethyl-1,7-octadiene-3-ol and 2,7-dimethyl-1,6-octadiene-3-ol in 76 % combined yield.



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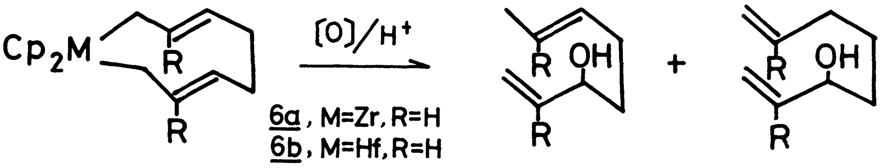
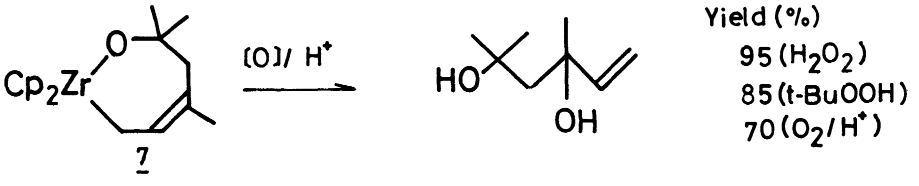


(6)

When an oxametallacycle 7 was used, a diol was obtained in good yield even by air oxidation followed by hydrolysis(eq. 7).



(7)

Above results tell us that when X in $Cp_2ZrX(R)$ is electron-withdrawing such as alkoxy, OH, OOH, or Cl, oxidation takes place prior to protonation. The present sequence of reactions provides a useful tool for organic synthesis especially for conversion of terpenes to terpene alcohols.10)

Iodination of organozirconium complexes was also examined to compare the mode of oxidation. Zr-isoprene and Zr-myrcene complexes liberated the diene in 72-75 % yield while $Cp_2Zr(2\text{-butenyl})_2$ gave 1-iodo-2-butene in 84 % yield and the complex 5 gave 1,6-diiodo-2,5,5-trimethyl-2-hexene in 86 % yield when two equimolar amounts of I_2 were added.11) Thus, the mode of halogenation of allylic zirconium complexes differs strikingly from that of oxidation with peroxides.

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5) Prepared by the 1:1 reaction of myrcene-magnesium, $(MgC_{10}H_{16})_n$, with Cp_2ZrCl_2 in essentially the same way as described for 1. See, H. Yasuda, Y. Nakano, K. Natsukawa, and H. Tani, Macromolecules, 11, 586 (1978).
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7) Prepared by reaction of 2,4-dimethylpentadienylpotassium with Cp_2ZrCl_2. ^1H-NMR at -30°C(toluene-d_8), δ 5.68(s, C_5H_5), 5.06(bs, CH_2), 4.49(s, CH), 1.97 and 1.76(CH_3), 1.47(bs, CH_2).
8) The structure was revealed to be $(C_5H_5)_2\overline{Zr(CH_2{\cdots}C(CH_3){\cdots}CH\text{-}CH_2)CRR'\text{-}C}H_2$ with reference to the X-ray data. Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda, and A. Nakamura, Chem. Lett., 1982, 1979.
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10) For example, A. A. Newman, "Chemistry of Terpenes and Terpenoids", Academic Press, London and New York, 1972.
11) The E/Z ratio was determined to be 82/18 from the ^1H-NMR spectrum($CDCl_3$), δ for the (E) isomer; 5.61(t, CH), 3.89(s, CH_2I), 3.08(s, CH_2I), 1.96(d, CH_2), 1.66(s, CH_3), 0.97(s, CH_3). δ for the (Z) isomer; 5.28(t, CH), 3.86(s, CH_2I), 3.10(s, CH_2I), 1.80(d, CH_2), 1.67(s, CH_3), 1.00(s, CH_3).

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