Osmium on Chelate Resin: Nonvolatile Catalyst for the Synthesis of Diols from Alkenes

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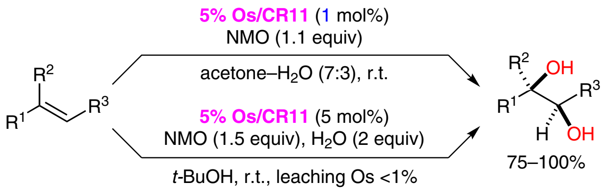

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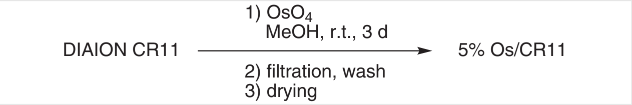
Abstract Osmium tetraoxide (OsO_4) was immobilized on a commercially available chelate resin DIAION CR11 (CR11) just by simply immersing it in a methanol solution of OsO_4 at room temperature. The resulting purple solid, 5% Os/CR11, indicated no volatility, and effectively catalyzed the oxidation of various alkenes to the corresponding diols.

Key words chelate resin, diols, osmium, oxidation, supported catalyst

The osmium tetraoxide (OsO_4)-catalyzed oxidation of alkenes in the presence of a stoichiometric amount of a co-oxidizing reagent, such as *N*-methylmorpholine *N*-oxide (NMO) and *tert*-butyl hydroperoxide (TBHP), is one of the most useful reactions for easy access to the corresponding 1,2-alkanediols.[1] OsO_4 (CAS registry number, 20816-12-0) is commercially available as an aqueous solution or a solid in a sealed ample due to its highly toxic and volatile nature. Thus, OsO_4 fundamentally possesses problems with its handling and safety that need to be solved. The immobilization of OsO_4 on supports is the usual solution to such problems, as represented by microencapsulated OsO_4 using polystyrene[2a] (MC OsO_4)[2b], phenoxyethoxymethylpolystyrene[3a,b] (PEM-MC OsO_4),[3c] and acryronitrile-butadiene-polystyrene[4] based on pioneering research by Kobayashi et al. Both organic materials, such as polystyrene derivatives (bearing ammonium salts,[5] imidazolium salts,[6] or amines[7]), polyaniline,[8] polysulfone,[9] PEG-polyvinyl pyridine,[10] polysiloxane,[11] polyacylquinine-acrylonitrile,[12] Amberlite,[13] and dendrimer[14] derivatives, and inorganic materials, such as silica gel,[15] zeolite,[16] molecular sieves,[17] aluminum-magnesium hydroxide layer,[18] and magnesium oxide,[19] have been used as supports of heterogeneous osmium catalysts.

Chelate resins have been used for the purification of water due to their metal-capturing ability based on the tight coordination (complexation) by some functional groups on the polymer backbone.[20] DIAION CR11 (CR11), which is a commercially available chelate resin manufactured by the Mitsubishi Chemical Corporation, possesses iminodiacetic acid moieties on the polystyrene-divinylbenzene-based polymer,[21] and the metal-CR11 complexes would be expected to be used as catalysts for organic reactions, since the CR11 is a proven and standardized industrial product with a stable supply. We have recently and successfully immobilized copper species on CR11 as a complex (12% Cu/CR11) and developed a solvent-free Huisgen triazole synthetic method using monosubstituted alkynes and azides.[22] In this paper, the application of the CR11 as the support for the preparation of osmium catalyst and its effective use for the oxidation of alkenes as a nonvolatile and easily prepared and handled catalyst are demonstrated.

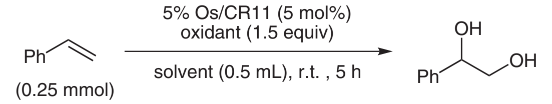
CR11 was immersed in a pale yellow solution of OsO_4 in methanol, and the mixture was gently stirred at room temperature under an argon atmosphere for three days. The solution turned green, blue, gray, and finally colorless, and the colorless CR11 was integrally empurpled, which was collected on the filter paper, washed with methanol, and dried under the reduced pressure (Scheme 1). The inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis of both the resulting filtrate and methanol wash detected a very low level of the residual osmium species [1 mg/L (only 0.13% of the original OsO_4 amount)]. This result indicated that the osmium species were nearly quantitatively supported on CR11, and the osmium content of the purple CR11 was determined to be 4.6 weight% (5% Os/CR11).[23,24]



Scheme 1 Simple and easy preparation of 5% Os/CR11

While the oxidation of styrene (250 μmol) as a substrate hardly proceeded in acetone (0.5 mL) for five hours in the presence of 5% Os/CR11 (5 mol%) and NMO (1.5 equiv vs. substrate) as a co-oxidant, the reaction efficiency was significantly improved by the addition of water (0.1–0.2 mL out of 0.5 mL, Table 1, entry 1 vs. entries 2–4).[25] Too much water (0.2 mL out of 0.5 mL) tended to decrease the yield of the desired diol (Table 1, entry 2). The reaction progress in *t*-BuOH as a solvent was also affected by the water use (Table 1, entries 5–8). The addition of two equivalents of water (to styrene, 500 μmol, 9.0 μL) in *t*-BuOH (0.5 mL) led to a highest yield of the desired product (Table 1, entry 8), while the reaction efficiency decreased by the addition of more water (Table 1, entries 6 and 7). Furthermore, the use of TBHP (70% in H_2O) or potassium ferricyanide instead of NMO was not effective for the present 5% Os/CR11-catalyzed oxidation in 70% aqueous acetone (Table 1, entries 9 and 10).

Table 1 Evaluation of Solvent and Oxidant for the 5% Os/CR11-Catalyzed Oxidation of Styrene

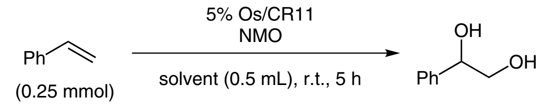


Entry	Solvent	Oxidant	Yield (%)[a]
1	acetone	NMO	trace
2	acetone–H_2O (6:4)	NMO	60
3	acetone–H_2O (7:3)	NMO	75
4	acetone–H_2O (8:2)	NMO	70
5	*t*-BuOH	NMO	74
6	*t*-BuOH–H_2O (8:2)	NMO	64
7	*t*-BuOH–H_2O (9:1)	NMO	74
8	*t*-BuOH–H_2O (2 equiv)[b]	NMO	81
9	acetone–H_2O (7:3)	TBHP	43
10	acetone–H_2O (7:3)	$K_3[Fe(CN)_6]$	0

[a] Determined by ^1H NMR using 1,3-benzodioxole as the internal standard.
[b] Conditions: 9.0 μL H_2O was used.

The appropriate use of both 5% Os/CR11 and NMO in 70% aqueous acetone as well as in *t*-BuOH was next investigated (Table 2). 5% Os/CR11 could be reduced to 0.8 mol% without a significant decrease in the reaction efficiency in 70% aqueous acetone (Table 2, entries 1–3), while the reaction became markedly suppressed by the reduction to 0.5 mol% (Table 2, entry 4). Furthermore, the use of NMO could also be decreased to 1.1 equivalents when using 1 mol% of 5% Os/CR11, and the desired diol was obtained in 89% yield (Table 2, entry 5). On the other hand, the use of the catalyst and NMO could hardly be reduced in *t*-BuOH regardless of the presence (2 equiv) or absence of water (Table 2, entry 7 vs. 8 and entry 9 vs. 10).

Table 2 Quantity of 5% Os/CR11 and NMO for the 5% Os/CR11-Catalyzed Oxidation of Styrene



Entry	Os (5%)/CR11 (mol%)	NMO (equiv)	Solvent	Yield (%)[a]
1	5	1.5	acetone–H_2O (7:3)	75
2	1	1.5	acetone––H_2O (7:3)	77
3	0.8	1.5	acetone–H_2O (7:3)	72
4	0.5	1.5	acetone–H_2O (7:3)	37
5	1	1.1	acetone–H_2O (7:3)	89 (82)[b]
6	1	1.0	acetone–H_2O (7:3)	74
7	5	1.5	*t*-BuOH	74
8	1	1.5	*t*-BuOH	41
9[c]	5	1.5	*t*-BuOH	81
10[c]	1	1.5	*t*-BuOH	41

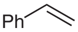
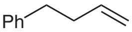
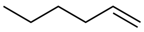
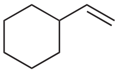
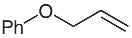
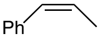
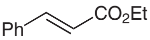
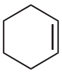
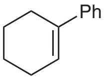
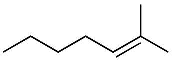
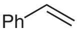
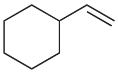
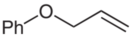
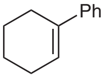
[a] Determined by ^1H NMR spectroscopy using 1,3-benzodioxole as the internal standard.
[b] Isolated yield is shown in parentheses.
[c] Conditions: 2 equiv of H_2O (9.0 μL) were added.

The substrate generality of the oxidation was confirmed by the combined use of 5% Os/CR11 (1 mol%) and NMO (1.1 equiv) in 70% aqueous acetone at room temperature (Table 3, entries 1–10).[26] Monosubstituted alkenes were good substrates, and the desired diols were obtained in excellent yields within short times (Table 3, entries 1–5). The reaction efficiency was also found to be quite high regardless of the geometry or cyclic/acyclic structure of the di- or trisubstituted alkenes (Table 3, entries 6–10). The 5% Os/CR11 indicated the same or a slightly more efficient catalyst activity compared to OsO_4 in 70% aqueous acetone (Table 3, entries 1, 5, and 9). The reaction conditions using *t*-BuOH as a solvent were also applicable to the dihydroxylation of various alkenes in the presence of H_2O (2 equiv) (Table 3, entries 11–14).[27]

The volatility of 5% Os/CR11 was next investigated in comparison to 4% aqueous OsO_4 using a similar technique reported by Kobayashi et al.[2a,3a] 5% Os/CR11 and 4% aqueous OsO_4 were separately placed in the bottom of short 5 mm diameter NMR tubes (ca. 11 cm length), and a piece of colorless cotton was stuffed ca. 6 cm above the bottom of each tube. Both tubes were closed with the cap and then sealed

Table 3 5% Os/CR11-Catalyzed Oxidation of Alkenes

$$\underset{\text{(0.25 mmol)}}{\text{alkene}} \xrightarrow[\text{70\% aq acetone (0.5 mL), r.t.}]{\text{5\% Os/CR11 (1 mol\%)}\ \text{NMO (1.1 equiv)}} \text{diol}$$

Entry	Alkene	Time (h)	Yield (%)[a]
1		5 (4)[b]	82 (78)[b]
2		5	95
3		4	85
4		3.5	100
5		4 (5)[b]	99 (81)[b]
6		8	85
7		21	75
8		5.5	82
9		5 (4)[b]	98 (94)[b]
10		6	75
11[c]		24	86
12[c]		24	82
13[c]		24	80
14[c]		24	89

[a] Isolated yield.
[b] Conditions: 4% aq OsO_4 was used instead of 5% Os/CR11.
[c] Conditions: The reaction was carried out using 5 mol% of 5% Os/CR11, 1.5 equiv of NMO, and 2 equiv of H_2O in *t*-BuOH.

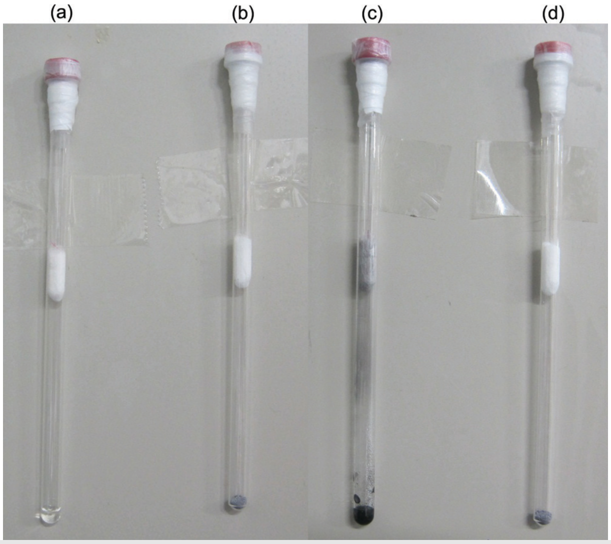
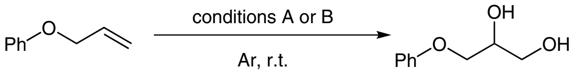


Figure 1 Volatility test of the 5% Os/CR11 and 4% aq OsO_4: (a) 4% aq OsO_4, 0 h; (b) 4% aq OsO_4, 2 weeks; (c) 5% Os/CR11, 0 h; (d) 5% Os/CR11, 2 weeks.

with Teflon tape (Figure 1, a and b). The cotton in the tube of 4% aqueous OsO_4 turned dark-gray within two weeks (Figure 1, c), while the cotton in the 5% Os/CR11 tube never changed in color even after at least six months (Figure 1, d). These results indicate that the 5% Os/CR11 has no volatile nature.

The reuse test of 5% Os/CR11 using allyl phenyl ether as a substrate either in 70% aqueous acetone (Table 4, conditions A) or in *t*-BuOH–H_2O (2 equiv, conditions B) unfortunately revealed that the yield of the desired diol slightly decreased in the second run and significantly decreased in the third run. Therefore, the leached osmium amount in the reaction media of the first run was then measured by ICP-AES. Although 71% osmium of the 5% Os/CR11 was leached into the reaction mixture under conditions A, it was found to be reduced to less than 1% in the case of conditions B (see Supporting Information).[28] Hence, the reaction could be carried out in *t*-BuOH–H_2O (2 equiv) with a low osmium leaching or in 70% aqueous acetone using only a small amount of 5% Os/CR11 (0.8–1 mol%), while the fresh catalyst should be used in the reaction system.

Table 4 Reuse Test of 5% Os/CR11



Run	Yield (%)[a] Conditions A[b]	Yield (%)[a] Conditions B[c]
1	100	86
2 (1st reuse)	87	79
3 (2nd reuse)	36	41

[a] Determined by ^1H NMR spectroscopy using 4-nitrotoluene as an internal standard.
[b] Conditions A: 5% Os/CR11 (1 mol%), NMO (1.1 equiv), 70% aq acetone, 4 h.
[c] Conditions B: 5% Os/CR11 (5 mol%), NMO (1.5 equiv), H_2O (2 equiv), *t*-BuOH, 24 h.

In conclusion, 5% Os/CR11 was readily prepared by only immersing the commercially available chelate resin CR11 in the methanol solution of OsO_4 at room temperature. A wide variety of alkenes were oxidized to the corresponding diols by the combined use of 5% Os/CR11 (0.8–5 mol%) as a catalyst and NMO (1.1–1.5 equiv) as a co-oxidant in 70% aqueous acetone or *t*-BuOH–H_2O (2 equiv). A disadvantage of use of 5% Os/CR11 is leaching of osmium to the reaction media, although the latter conditions could reduce the leaching level to less than 1% of used osmium amount. 5% Os/CR11 could be stored in a regular screw-capped vial under air without volatilization. The facile preparation, high catalyst activity, and easy operation of 5% Os/CR11 together with the general and reliable quality of CR11 would be a substitute for OsO_4 as a catalyst for the oxidation of alkenes.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1379990.

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(21) Homepage for DIAION of Mitsubishi Chemical Co., see http://www.diaion.com/en/.

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(23) **Preparation of 5% Os/CR11**
To a solution of OsO_4 (1.00 g, 3.93 mmol) in MeOH (600 mL) was added DIAION CR11 (40.3 g, H_2O ca. 60–65%), and the mixture was stirred at r.t. under an Ar atmosphere for 3 d. The resulting purple resin was collected on a filter paper, washed with MeOH (3 × 100 mL), then dried under reduced pressure to give 5% Os/CR11 (16.3 g). The filtrate and MeOH wash were diluted to 1 L with MeOH in a volumetric flask. The inductively coupled plasma atomic emission spectrometry (ICP-AES) of the combined filtrate and MeOH wash detected 1 mg/L of osmium species (1 mg Os in 1 L MeOH), indicating that 746.6 mg Os was embedded on the CR11 [3.93 mmol × 190.23 (molecular weight of Os) – 1 mg (Os in MeOH)]. Therefore, the amount of Os on CR11 was determined to be ca. 5 weight% osmium [746.6 (mg, weight of Os) ÷ 16300 (mg, weight of catalyst) × 100 = 4.6%].

(24) The immobilization manner of osmium to CR11 was not characterized.

(25) Water should be necessary for the hydrolysis of the intermediary osmate ester, which is supposedly obtained by the cycloaddition reaction of osmium species with an alkene.

(26) **General Procedure for the 5% Os/CR11-Catalyzed Oxidation of Alkenes in 70% Aqueous Acetone**
A mixture of the alkene (250 μmol), NMO (32.2 mg, 275 μmol), and 5% Os/CR11 (9.5 mg, 2.50 μmol) in 70% aq acetone (500 μL) was stirred under an Ar atmosphere at r.t. After the consumption of the alkene (TLC analysis), the 5% Os/CR11 was removed by filtration, and the filtrate was concentrated in vacuo. The residue was passed through a short silica gel column chromatography to give the corresponding diol. The NMR data of the products were identical to those in the literature, see the Supporting Information.

(27) **General Procedure for the 5% Os/CR11-Catalyzed Oxidation of Alkenes in *t*-BuOH**
A mixture of the alkene (250 μmol), NMO (43.9 mg, 375 μmol), 5% Os/CR11 (47.6 mg, 12.5 μmol), and H_2O (9.0 μL, 500 μmol) in *t*-BuOH (500 μL) was stirred under an Ar atmosphere at r.t. After

24 h, the 5% Os/CR11 was removed by filtration, and the filtrate was concentrated in vacuo. The residue was passed through a short silica gel column chromatography to give the corresponding diol.

(28) It is not clear why satisfactory reuse of 5% Os/CR11 was not achieved even under conditions B where only a small amount of osmium was leached out from the catalyst, although the decrease of each run in the catalyst activity was lower than that under conditions A.