SHORT PAPER

J. Chem. Research (S),
2002, 400–402

Highly efficient oxidation of alcohols catalysed by Nafion-cerium(IV) or Nafion-chromium(III)[†]

Takehiko Yamato[*] and Naoki Shinoda

Department of Applied Chemistry, Faculty of Science and Engineering, Saga University,
Honjo-machi 1, Saga-shi, Saga 840-8502, Japan

Ce(IV) or Cr(III) impregnated Nafion-K catalyst is found to be effective in promoting the dehydrogenative oxidation of primary and secondary alcohols to aldehydes or ketones with $NaBrO_3$ as a co-oxidant.

Keywords: oxidation, alcohol, impregnated Nafion-K catalyst, co-oxidant

Environmental constraints are incentives to the development of catalytic procedures using clean oxidants.[1] The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is one of the most important reactions in organic chemistry. It is often carried out with large excesses of chromates or manganates.[2] Although these procedures are usually very effective, they lead to stoichiometric amounts of toxic co-products. The operation is frequently tedious and reaction conditions are generally quite critical. The reaction requires either prolonged periods of standing or elevated temperatures for its completion. In addition, the formation of gummy precipitates and troublesome workup are also serious problems arising from using chromium(VI) reagents for the oxidation of alcohols. In order to overcome these difficulties, polymer reagents such as poly(vinylpyridinium chlorochromate)[3] or poly(vinylpyridinium dichromate)[4] have been introduced. Although the purification of the final product is easy, the exchange capacity of the polymer oxidants is usually low. Furthermore, the recycling of reagents requires troublesome steps of work-up. On the other hand, Kanemoto *et al.* reported that *tert*-butylhydroperoxide oxidises alcohols to the corresponding carbonyl compounds (71–98%) effectively with a Cr(III) or Ce(IV) impregnated Nafion-K catalyst, which is reusable after simple washing.[5] Recently, we have found that Nafion-H catalyst, a perfluorinated sulfonic acid resin,[6] is effective in a wide range of liquid and gas phase reactions, including electrophilic substitutions on aromatic nuclei, transalkylations, condensations, *etc.*[7]

Now we report an efficient and convenient procedure for the oxidation of primary and secondary alcohols to aldehydes or ketones with Cr(III) or Ce(IV) impregnated Nafion-K catalyst using $NaBrO_3$ as a co-oxidant, which proceeds quite readily, giving quantitative yields.

Results and discussion

Oxidation of adamantan-2-ol (**1**) with a Ce(IV) or Cr(III) impregnated Nafion-K catalyst was carried out in the presence of the co-oxidant, $NaBrO_3$. The results are compiled in Table 1. The attempted oxidation of adamantan-2-ol (**1**) with Ce(IV) impregnated Nafion-K catalyst led only to the recovery of the starting compound in quantitative yield in spite of using two equivalents of co-oxidant. Increasing the amounts of $NaBrO_3$ only led to the recovery of the starting compound. This result suggested that the present oxidation system dramatically reduced the catalytic activity of Nafion-Ce(IV) and that the regeneration of the Nafion-Ce(IV) oxidant with co-oxidants in the reaction system did not work well. In contrast, in the presence of a Cr(III) impregnated Nafion-K catalyst the oxidation product, 2-adamantanone (**2**) was obtained in 12% yield together with recovery of the starting compound. This finding suggests that the Nafion-Cr(III) oxidation system is much stronger than Nafion-Ce(IV) system. Prolonging the reaction time for 24 h resulted the increase of the yield of **2** from 12 to 45%. Consequently, although the yields of oxidation product are low, Cr(III) impregnated Nafion-K catalyst was found to be effective in promoting the dehydrogenative oxidation of adamantan-2-ol (**1**) with $NaBrO_3$ as a co-oxidant.

When the recovered Nafion-Cr was used under the same reaction conditions, no oxidation product was obtained. This result indicates that the catalytic system which reduced the Cr could not regenerate the Cr(III) by using the $NaBrO_3$ in the system. A remarkable deactivation of the catalyst was observed because regeneration of the catalyst could not be achieved to the original catalytic activity. On the other hand, in acidic media $NaBrO_3$ smoothly oxidises the Ce(III) to Ce(IV). Similarly, in acidic media Nafion-Ce(IV) could be regenerated in the present oxidation system. In fact, when the oxidation of adamantan-2-ol (**1**) with Nafion-Cr(III) in the presence of $NaBrO_3$ with 1 M of nitric acid was carried out in refluxing $MeCN/H_2O$ for 6h, the yield of the desired 2-adamantanone (**2**) increased from 12% to quantitative. It was also found that the addition of 10 wt % of Nafion-H as a co-catalyst to the dual oxidation system, *e.g.* Nafion-Ce(IV)-$NaBrO_3$ or Nafion-Cr(III)-$NaBrO_3$ instead of nitric acid, also increased the yield of adamantanone **2** to quantitative and shortened the reaction time. In the case of Nafion-Cr(III) under reflux, it takes only 2 h to complete the reaction to afford 2-adamantanone (**2**) in quantitative yield. Nafion-Ce(IV) or Nafion-Cr(III) were recovered simply by filtering the hot reaction mixture and the catalyst

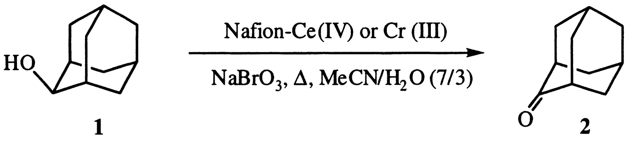


Table 1 Oxidation of adamantan-2-ol **1** with Nafion-Ce(IV) or Nafion-Cr(III) using a dual oxidant system[a]

Run	Catalysts	Time/h	Yield/%[b]
1	Nafion-Ce	6	0
2	Nafion-Cr	6	12
3	Nafion-Cr	24	45
4	Nafion-Ce Nafion-H	6	100 [90][c]
5	Nafion-Cr Nafion-H	2	100 [92][c]

[a]Reaction conditions: [$NaBrO_3$/**1**] = 2:1; Nafion-Ce(IV), Cr(III) 20 wt%; Nafion-H 10 wt%. [b]Yields are determined by GLC analysis. [c]Isolated yields are shown in parentheses.

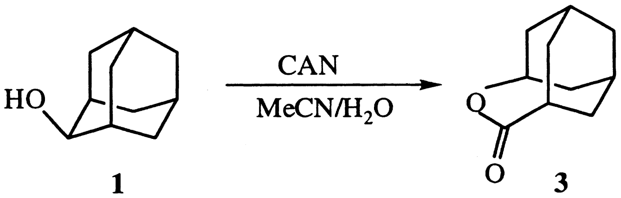
---

[*] To receive any correspondence. E-mail: yamatot@cc.saga-u.ac.jp

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

was readily regenerated without loss of catalytic activity. The reaction was very clean. The amount of catalyst required, as a function of the amount of adamantan-2-ol (**1**), was between 5 and 20 wt%. Optimum yields of 2-adamantanone (**2**) were obtained with 20 wt% of catalyst. The use of 5 wt% of catalyst gave lower yields.

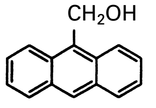
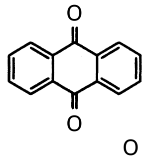
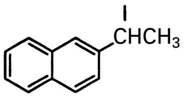
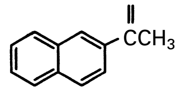
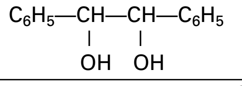
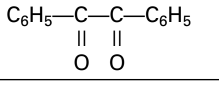
It should be emphasised that bromate ion itself is not capable of oxidising adamantan-2-ol (**1**) since the attempted oxidation of **1** with $NaBrO_3$ in the absence of Nafion-Ce(IV) or Nafion-Cr(III) under the same reaction conditions described above resulted in the recovery of the starting compound. Thus, the present oxidation system must be mediated by Nafion-cerium (IV) or Nafion-chromium (III) species. As shown in Table 1, the present method provides good yields with easy isolation of the products. No concomitant Baeyer–Villiger product was observed under the reaction conditions in contrast to the direct oxidation of adamantan-2-ol (**1**) with excess of ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$; CAN], which gives **3** in good yield.[8–10]



1 **3**

The presently developed oxidation systems were further applied to benzyl alcohols to afford benzaldehydes and ketones. As shown in Table 2, the present method provides good yields, easy isolation of the products and is compatible with the presence of methyl, bromo or nitro substituents on the aryl group. Furthermore no concomitant debromination and demethylation were observed under the reaction conditions. However, oxidation of 9-hydroxymethyl of anthracene to afford 9-formylanthracene failed. Only 9,10-anthraquinone was obtained in 90% yield. Similar results were obtained in the oxidation of benzyl alcohols with Cr(III) impregnated Nafion-K catalyst in the presence of co-oxidant $NaBrO_3$. No formation of benzoic acid was observed under the reaction conditions used. On the other hand, oxidation of *p*-methylbenzyl alcohol with Ce (IV) or Cr(III) impregnated Nafion-K catalyst in the presence of *tert*-butylhydroperoxide (70%) in benzene under reflux led to a mixture of *p*-methylbenzaldehyde and *p*-methylbenzoic acid.

Table 2 Oxidation of benzyl alcohols with Nafion-Ce(IV)/Nafion-H/$NaBrO_3$[a]

Run	Alcohol	Product	Yield/%[b]
1	$C_6H_5CH_2OH$	C_6H_5CHO	90
2	$4\text{-}MeC_6H_4CH_2OH$	$4\text{-}MeC_6H_4CHO$	95
3	$4\text{-}BrC_6H_4CH_2OH$	$4\text{-}BrC_6H_4CHO$	82
4	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CHO$	87
5			90
6			80
7	 $C_6H_5\text{—}\underset{OH}{\underset{\mid}{CH}}\text{—}\underset{OH}{\underset{\mid}{CH}}\text{—}C_6H_5$	 $C_6H_5\text{—}\underset{O}{\underset{\|}{C}}\text{—}\underset{O}{\underset{\|}{C}}\text{—}C_6H_5$	70

[a]Reaction conditions: [$NaBrO_3$]/[Aryl alcohols] = 2:1; Nafion-Ce(IV) 20wt%; Nafion-H 10wt%; Solvent: aqueous acetontrile (7:3 v/v); Reaction time: 4h; Reaction temp.: reflux. [b]Isolated yields are shown.

In conclusion, the Cr(III) or Ce(IV) impregnated Nafion-K catalyst oxidation method overcomes the formation of gummy precipitates and troublesome work-up which are serious problems arising from the use of stoichiometric chromium(VI) reagents for oxidation of alcohols. Furthermore, the present oxidation method provides excellent yields, easy isolation of products, and ready regeneration of the catalyst without the loss of catalytic activity because the real oxidising agent is $NaBrO_3$.

Experimental

^1H NMR spectra were recorded at 270 MHz on a Nippon Denshi JEOL FT-270 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct-inlet system. G.L.C. analyses were carried out by a Shimadzu gas chromatograph, GC-14A (conditions: Silicone OV-1, 2 m; programmed temperature rise, 12°C/min; carrier gas nitrogen, 25 cm^3/ min.).

Materials: Nafion-H catalyst was prepared from commercially available (DuPont) Nafion-K resin, as previous described.[6,7] Preparation of Nafion-Ce (IV) or Nafion-Cr (III) was carried out following the reported procedures.[5] Nafion-Ce(IV) was prepared as follows. Nafion-K (1.1 g) was stirred with a solution of $(NH_4)_2Ce(NO_3)_6$ (1.75 g) in deionised water (30 cm^3) for 36 h at 25°C. The catalyst was filtered, washed with water (10 $cm^3 \times 5$) and dried to constant weight. Titrations of the polymers thus prepared indicated capacities of 0.54 mmol of Ce(IV) per gram which correspond to 71% of the theoretical capacity (0.94 mmol/g) of a fully loaded resin. Similarly, Nafion-Cr(III) was prepared from Nafion-K and $Cr(OAc)_3$.

General Procedure for Nafion-Ce(IV)- or Nafion-Cr(III)-catalysed oxidation of alcohols with $NaBrO_3$: A mixture of adamantan-2-ol (**1**) (152 mg, 1 mmol) and 30 mg (20 wt%) of Nafion-Ce(IV), and $NaBrO_3$ (302 mg, 2 mmol) in a mixture of acetonitrile (10 cm^3, 7:3 v/v) and 15 mg (10 wt%) of Nafion-H was refluxed until completion of the reaction as monitored by GLC analysis. After 6 h, the solid resin was filtered off and the filtrate was extracted with CH_2Cl_2 (10 $cm^3 \times 2$) and washed with water (5 $cm^3 \times 2$). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure to give a colourless solid, which was recrystallised from hexane to yield 2-adamantanone (**2**) (135 mg, 90%) (m.p. 255–257°C, lit.[11] 256–258°C).

General procedure for Nafion-Ce(IV)-catalysed oxidation of arylalcohols with $NaBrO_3$: A mixture of *p*-methylbenzyl alcohol (122 mg, 1 mmol) and 25 mg (20 wt%) of Nafion-Ce(IV), and $NaBrO_3$ (302 mg, 2 mmol) in a mixture of acetonitrile (10 cm^3, 7:3 v/v) and 12 mg (10 wt%) of Nafion-H was refluxed for 4 h. The solid resin was filtered off and the filtrate was extracted with CH_2Cl_2 (10 $cm^3 \times 2$) and washed with water (5 $cm^3 \times 2$). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure to give *p*-methylbenzaldehyde (114 mg, 95%) as a colourless liquid. The product was also identified by the melting point of its 2,4-dinitrophenylhydrazone [m.p. 232–234°C (lit.[12] 233°C)].

Products in Table 2: Products were identified by comparison of melting points with those reported in the literature.[11] In the case of run 1 benzaldehyde was isolated as benzaldehyde 2,4,-dinitrophenylhydrazone, m.p. 238–240°C (lit.[11] 239–241°C). The purity of the isolated products was determined by GLC.

Regeneration of spent catalyst. – The spent catalyst was washed several times with acetone and deionised water and then it was dried at 105°C for 10 h. The activity of the regenerated catalyst was identical to that of fresh catalyst.

We thanks to Professor George A. Olah and Professor G.K.S. Prakash (Hydrocarbon Research Institute, University of Southern California) for giving us an opportunity to carry out the present project and for the supply of Nafion-H reagent.

Received 4 December 2001; accepted 1 April 2002
Paper 01/1170

References

1 (a) C. Piancatelli, A. Scettri and M. D'Auria, *Synthesis*, 1982, 245; (b) F.A. Luzzio and F.S. Guziec, *Org. Prep. Proced. Int.*, 1988, **20**, 533.
2 J. Muzart, *Chem. Rev.*, 1992, **92**, 113.
3 J.M.J. Fréchet, J. Warnock and M.J. Farrall, *J. Org. Chem.*, 1978, **43**, 2613.
4 (a) J.M.J. Fréchet, P. Darling and M.J. Farrall, *J. Org. Chem.*, 1981, **46**, 1728; (b) G. Cardillo, M. Orend and S. Sandri, *J. Am. Chem. Soc.*, 1976, **98**, 6737.
5 S. Kanemoto, H. Saimoto, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 3317.
6 G.A. Olah, P.S. Iyer and G.K.S. Prakash, *Synthesis*, 1986, 513.
7 T. Yamato, *J. Synth. Org. Chem. Jpn.* 1995, **53**, 487 and references therein.
8 L. Ho, *Synthesis*, 1973, 347.
9 J. Muzart and A.N. Ajjou, *Synthesis*, 1993, 785.
10 P. Soucy, T.L. Ho and P. Deslongchamps, *Can. J. Chem.*, 1972, **50**, 2047.
11 *Dictionary of Organic Compounds*, Oxford University Press: London, 1978.
12 S.K. Srimany and B. Chaudhury, *J. Chem. Soc.*, 1961, 4576.