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Cr(III) OR Ce(IV) IMPREGNATED PERFLUORINATED RESIN-SULFONIC ACID CATALYST FOR THE OXIDATION OF ALCOHOLS

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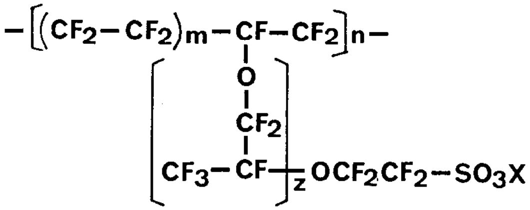
Abstract: Several polymer supported catalysts are prepared by treatment of Nafion® 511 (abbreviated as NAFK below) with metal salts and found to be effective in promoting the dehydrogenative oxidation of alcohols with $^{t}BuOOH$.

The formation of gummy precipitate and troublesome workup are serious problems arising from using chromium(VI) reagents for stoichiometric reagents for the oxidation of alcohols. In order to overcome these difficulties, polymer reagents such as poly(vinylpyridinium chlorochromate)[1] or poly(vinylpyridinium dichromate)[2] have been introduced.[3] Although the purification of the final products is easy, the exchange capacity of the polymer oxidants is usually low. Furthermore recycling of reagents requires troublesome steps of workup. Here we wish to report that *t*-butylhydroperoxide oxidizes alcohols into the corresponding carbonyl compounds effectively under Cr(III) or Ce(IV) impregnated NAFK[4] catalyst, which is reusable after simple washing.



Nafion®511: X = K (NAFK)
Cr/NAFK: X = Cr(III)
Ce/NAFK: X = Ce(IV)

Polymer supported catalysts (Cr(III)/NAFK and Ce(IV)/NAFK) were prepared as follows. NAFK (1.1 g) was stirred with a solution of $Cr(OAc)_3$ (0.69 g) or $(NH_4)_2Ce(NO_3)_6$ (1.75 g) in deionized water (30 ml) for 36 h at 25°C. The catalyst was filtered, washed with water (10 ml x 5) and dried to constant weight. Titrations of the polymers thus prepared indicated capacities of 0.68 mmol of Cr(III) and 0.54 mmol of Ce(IV) per gram which correspond to 75% and 71% of the theoretical capacity (0.94 mmol/g) of a fully loaded resin.

A solution of 1-phenylethanol (0.12 g, 1.0 mmol) in chlorobenzene (2.0 ml) was added to a suspension of Cr/NAFK (50 mg) in chlorobenzene (1.0 ml). Then a solution of _t_-butylhydroperoxide in benzene[5] (2.64 M, 1.5 ml, 4.0 mmol) was added and the whole was heated at 85°C for 6-8 h. The solid catalyst was filtered off and washed with AcOEt. The filtrate and washings were combined and washed with aq. $NaHSO_3$ and brine. Purification of the concentrated residue by silica gel column chromatography gave acetophenone (0.11 g) in 95% yield. The recovered catalyst was dried and reused without loss of Cr(III) ion. 1-Phenylethanol was oxidized to acetophenone repeatedly (first run, 95% yield, and second run with the recovered reagent, 92%).

As shown in Table 1, secondary alcohols were easily transformed into the corresponding ketones in fair to good yields. Meanwhile, primary alcohols gave complex mixtures under the same reaction conditions.[6]

Table 1. Oxidation of alcohols with Cr/NAFK-^{t}BuOOH system[a,b)]

Alcohol	Yield(%) of Carbonyl Compound	Alcohol	Yield(%) of Carbonyl Compound
Cyclododecanol	86	4-_t_-Butylcyclohexanol	81
$PhCH=CHCH(OH)CH_3$	81	Carveol	82
4-Dodecanol	81	$PhCH(OH)CH_3$	95
_p_-$Cl-C_6H_4CH(OH)CH_3$	93	Ph_2CHOH	98

a) ^{t}BuOOH (4.0 mmol) and Cr/NAFK (50 mg, 0.034 mmol) were employed per one mmol of alcohol. b) Yields represent isolated, purified products.

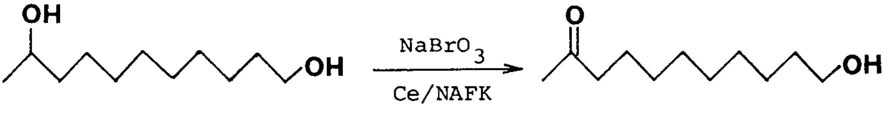
Table 2. Oxidation of alcohols with Ce/NAFK-^{t}BuOOH system[a,b)]

Alcohol	Yield(%) of Carbonyl Compound	Alcohol	Yield(%) of Carbonyl Compound
Cyclododecanol	82	4-_t_-Butylcyclohexanol	98
2-Cyclododecen-1-ol	82	Carveol	98
4-Dodecanol	71	$PhCH(OH)CH_3$	93
3-Undecanol	79	11-Dodecen-2-ol	80

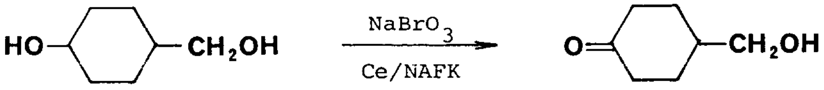
a) The hydroxy compounds (1.0 mmol), ^{t}BuOOH (4.0 mmol), and Ce/NAFK (50 mg, 0.027 mmol) were combined in benzene and the mixture was stirred for 6 h at 80°C. b) Isolated yields.

Ce(IV)/NAFK-^{t}BuOOH system has proved to be effective oxidant of alcohols. Carveol (0.15 g, 1.0 mmol) and ^{t}BuOOH (3.09 M, 1.3 ml, 4.0 mmol) were added to a suspension of Ce(IV) supported polymer (50 mg) in benzene (4.0 ml). The resulting mixture was stirred for 2 h at 80°C. Workup and purification as described above gave carvone (0.15 g) in 98% yield.

Other results are found in Table 2. In contrast to the previously reported $(NH_4)_2Ce(NO_3)_6$-$NaBrO_3$ system,[7] this new method was not affected by the olefinic moiety in the substrates. Thus, 2-cyclododecen-1-ol and 11-dodecen-2-ol gave the corresponding ketones in good yields upon treatment with Ce/NAFK-^{t}BuOOH system. A primary alcohol such as 1-dodecanol was recovered practically unchanged. Selective oxidation of secondary hydroxyls in the presence of primary ones has been achieved as shown below. The reactions were performed with $NaBrO_3$ as a co-oxidant in AcOH at 55°C and the reactions completed within 3 h.[8]



82% (Ref. 9)



73% (Ref. 10)

The Cr(III) and Ce(IV) catalysts prepared from Nafion®-H (NAFH)[11] also were effective for the transformation of alcohols into carbonyl compounds, but the products were contaminated by the di-*t*-butyl acetals which are ascribed to the NAFH catalyzed acetalization of the ketones.[12] Metals such as Cu(II), Ni(II) and Mn(II) supported on the resins were not so effective as Cr(III) or Ce(IV). The starting alcohols were only partly (at most 30%) converted into ketones under the same reaction conditions.[13,14]

References and Notes

1. J. M. J. Fréchet, J. Warnock, and M. J. Farrall, *J. Org. Chem.*, **43**, 2613 (1978).
2. J. M. J. Fréchet, P. Darling, and M. J. Farrall, *ibid.*, **46**, 1728 (1981). A use of CrO_4H^- form of Amberlyst A-26, a macroreticular anion exchange resin, has been also reported. G. Cainelli, G. Cardillo, M. Orend, and S. Sandri, *J. Am. Chem. Soc.*, **98**, 6737 (1976).
3. Recently we have reported another solution of these problems by the use of $Me_3SiOOSiMe_3$ as a co-oxidant in the presence of catalytic amount of

pyridinium dichromate. S. Kanemoto, K. Oshima, S. Matsubara, K. Takai, and H. Nozaki, *Tetrahedron Lett.*, **24**, 2185 (1983).

4. Nafion is a registered trademark of E. I. du Pont de Nemours & Co. See J. D. McMlure and S. G. Brandenberger, U. S. Patent, 4,038,213 (1977). Recent reports on Nafion reagents in organic synthesis: S. Murata and R. Noyori, *Tetrahedron Lett.*, **21**, 767 (1980); H. Saimoto, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **56**, 3078 (1983); G. A. Olah, S. C. Narang, R. Malhotra, and J. A. Olah, *J. Am. Chem. Soc.*, **101**, 1805 (1979). We thank Mitsui Fluorochemical Co. for a generous gift of NAFK.
5. G J. G. Hill, B. E. Rossiter, and K. B. Sharpless, *J. Org. Chem.*, **48**, 3607 (1983).
6. For instance, treatment of 1-dodecanol with ^{t}BuOOH in the presence of Cr/NAFK gave a complex mixture containing dodecanal (39%) and dodecanoic acid (15%) after heating at 80°C for 12 h. Starting material was also recovered (24%).
7. H. Tomioka, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **23**, 537 (1982).
8. With Ce/NAFK-^{t}BuOOH system, the reaction was very sluggish and the desired products were contaminated by a couple of unidentified by-products.
9. Mp 42-43°C; IR (neat) 3424, 1709, 1358, 1042 cm^{-1}; NMR (CCl_4) δ1.1-1.8 (m, 14H), 2.09 (s, 3H), 2.36 (t, J = 6.6 Hz, 2H), 3.58 (t, J = 6.8 Hz, 2H), 3.78 (b, 1H). Found: C, 70.65; H, 11.90%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%.
10. Bp 149-152°C (bath temp, 20 Torr); IR (neat) 3400, 1714, 1165, 1084, 1034 cm^{-1}; NMR (CCl_4) δ 1.1-2.7 (m, 10H), 3.63 (d, J = 3.0 Hz, 2H).
11. NAFK was converted into the H^+ form according to the reported procedure. J. Kaspi and G. A. Olah, *J. Org. Chem.*, **43**, 3142 (1978).
12. Oxidation of 4-*t*-butylcyclohexanol with Ce(IV)/NAFH-^{t}BuOOH gave cyclohexanone (30%) along with cyclohexanone di-*t*-butyl acetal (52%). Coexistence of $NaHCO_3$ improved the yield of cyclohexanone (68%) and reduced the formation of acetal (7%).
13. The present work has its origin in the finding that 4-methyl-1-phenyl-2-pentyne-1,4-diol is converted into the corresponding ynone quantitatively on treatment with NAFH in 70% aqueous ^{t}BuOOH. H. Saimoto, M. Shinoda, S. Matsubara, K. Oshima, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **56**, 3088 (1983). We are grateful to Dr. Tamejiro Hiyama for helpful discussion.
14. Financial support by the Ministry of Education, Science, Culture, Japanese Government (Grant-in-Aid for Scientific Research 5811105 and 58550566) is acknowledged.

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