

domain of SBR or SBR-P than in those of other resins. The higher effective pH in the microdomain of SBR or SBR-P, therefore, does not appear to be directly related to the enhanced yield of the methylation reaction in the presence of these resins.

Alkylation of phenolate anions is involved in the preparation of many pharmaceuticals. The anion-exchange resins are cheap, and separation of the catalyst from the products is very simple when the resins are used. Thus, ion-exchange resins may have wide applications in various synthetic reactions, especially on industrial scales.

Acknowledgement. This work was supported by a grant (1988) from Korea Research Foundation.

References

1. T. Kunitake and S. Shinkai, *Adv. Phys. Org. Chem.*, **17**, 435 (1980).
2. (a) J. Suh, I. S. Scarpa, and I. M. Klotz, *J. Am. Chem. Soc.*, **98**, 7060 (1976); (b) J. Suh and I. M. Klotz, *Bioorg. Chem.*, **6**, 165 (1977); (c) J. Suh and I. M. Klotz, *J. Polymer Sci. Pol. Chem. Ed.*, **16**, 1943 (1978); (d) J. Suh and I. M. Klotz, *J. Am. Chem. Soc.*, **106**, 2373 (1984).
3. D. C. Sherrington, "Polymer-supported Reactions in Organic Synthesis", P. Hodge and D. C. Sherrington, Eds., Wiley, New York (1980), Chapter 3.
4. J. Suh and Y. H. Yoon, *Bull. Korean Chem. Soc.*, **6**, 249 (1985).
5. J. Suh and Y. H. Yoon, *Bull. Korean Chem. Soc.*, **10**, 214 (1989).
6. J. Suh and B. S. Mun, *J. Org. Chem.*, **54**, 2009 (1989).
7. R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Wagborne, *J. Am. Chem. Soc.*, **94**, 1148 (1972).
8. R. A. Y. Jones, "Physical and Mechanistic Organic Chemistry", 2nd Edn., Cambridge University Press, Cambridge (1984), Chapter 5.

Oxidation of Alcohols with NiO₂-Al₂O₃

Kwan Soo Kim*, Sung Bum Cho, and Chi Sun Hahn

Department of Chemistry, Yonsei University,
Seoul 120-749

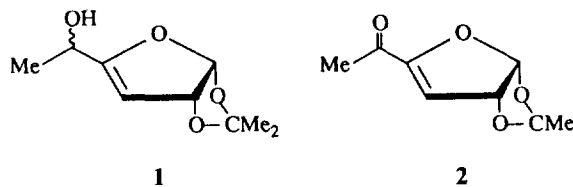
Received November 12, 1990

Selective oxidation of allylic and benzylic hydroxy groups in the presence of aliphatic hydroxy groups is a useful transformation in organic synthesis. Although there are several reagents available for this purpose, these oxidizing agents do not show sufficient selectivity, or are not generally applicable, or are not readily available. For example, the widely used manganese dioxide oxidizes aliphatic alcohols in certain cases.¹ Even chromium (VI) reagents such as bis(tetrabutylammonium)dichromate² and 4-dimethylaminopyridinium chlorochromate,³ which have recently reported and were

Table 1. Oxidation of Benzylic and Allylic Alcohols with NiO₂-Al₂O₃ in Benzene

Alcohols	Products	Time, h	Yield, % ^{a,b}
benzyl alcohol	benzaldehyde	3	98
sec-phenethyl alcohol	acetophenone	3	97
p-anisyl alcohol	p-anisaldehyde	5	(85)
benzhydrol	benzophenone	2	(95)
allyl alcohol	acrolein	3	98
3-buten-2-ol	3-buten-2-one	2	98
crotyl alcohol	crotonaldehyde	3	99
cinnamyl alcohol	cinnamaldehyde	3	98
geraniol	geranial	6	85
1	2	2	(90)

^a The yields were determined by GC. ^b The yields in parentheses are isolated ones.



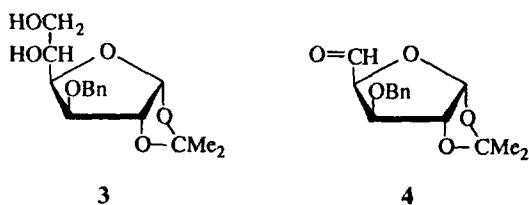
claimed to be superior to other selective oxidizing agents, still oxidize saturated primary and secondary alcohols to a significant extent. We have also reported that potassium ferrate,⁴ potassium ruthenate,⁵ and potassium manganate⁶ under phase-transfer catalysis conditions selectively oxidizes allylic and benzylic alcohols. Although nickel peroxide, NiO₂, has been known as an oxidizing agent for a long time⁷ and has been used for the oxidation of alcohols,⁸ its utility has been limited in organic synthesis because it has not shown advantages over versatile manganese dioxide, MnO₂. Another reason for the limited utility of nickel peroxide is its insolubility in organic solvents. This problem, however, can be overcome by employing heterogeneous reactions on solid supports. In this communication, we report that a solid mixture of nickel peroxide⁹ and Woelm 200 basic chromatographic alumina¹¹ is a more efficient and selective oxidizing system for allylic and benzylic alcohols than the most widely used manganese dioxide. We have also found that NiO₂-Al₂O₃ system cleaves vicinal diols.

The oxidation on the solid support in the present work was performed by stirring the benzene solution (10 ml) of an alcohol (1.00 mmol) with the solid mixture¹¹ of nickel peroxide (0.46 g, 1.50 mmol) and Al₂O₃ (W-200-B) (0.46 g) at room temperature under nitrogen. After completion of the reaction, the solid reagent was removed by the filtration and evaporation of the solvent afforded the product. Benzyl alcohol was readily oxidized to benzaldehyde by this solid oxidizing agent in 2 h in 98% yield. Other benzylic alcohols were similarly transformed into the corresponding aldehydes or ketones in high yields as shown in Table 1. NiO₂-Al₂O₃ system was also effective for the oxidation of allylic alcohols to the corresponding α , β -unsaturated aldehydes or ketones. On the other hand, aliphatic primary and secondary alcohols such as 1-decanol, 1-dodecanol, 4-phenylcyclohexanol, and 2-heptanol were not oxidized by NiO₂-Al₂O₃ in prolonged reaction time at higher reaction temperature. Table 1 clearly

Table 2. Oxidative Cleavage of Vicinal Diols with NiO₂-Al₂O₃ in Benzene at 50°C

Diols	Products	Time, h	Yield, % ^{a,b}
<i>trans</i> -1,2-cyclohexanediol	1,6-hexanedial	5	75
1-phenyl-1,2-ethanediol	benzaldehyde + formaldehyde	5	98
1,2; 5,6-di-O-isopropylidene-D-glycer-	1,2-O-isopropylidene-D-glycer-aldehyde	14	52
3	4 + formaldehyde	10	(43)

^a The yields were determined by GC. ^b The yields in parentheses are isolated ones.



indicates that NiO₂-Al₂O₃ system oxidizes benzylic and allylic alcohols to the corresponding aldehydes or ketones in shorter reaction time and in much higher yield than either activated MnO₂ or NiO₂ alone. For example, NiO₂-Al₂O₃ oxidizes geraniol to geranial in 85% in 6 h at room temperature whereas MnO₂ oxidizes geraniol to geranial in 50% in 90 h at 50°C.¹² Efficiency of NiO₂-Al₂O₃ system was more clearly shown in the oxidation of a carbohydrate allylic alcohol **1**. Oxidation of allylic alcohol **1** to ketone **2** was sluggish with activated MnO₂ or NiO₂ alone. Other various oxidizing agents such as PCC, PDC, and KMnO₄ under phase-transfer condition were not efficient and provided complex mixtures of products in certain cases. NiO₂-Al₂O₃ system efficiently oxidized compound **1** to its ketone **2** in 90% yield.

NiO₂-Al₂O₃ system also cleaved vicinal diols as shown in Table 2. 1-Phenyl-1,2-ethanediol was converted to benzaldehyde and formaldehyde in 98% yield in benzene at 50°C. At room temperature, however, quite long reaction time was required and the yield was substantially lowered. 1,2,5,6-Di-O-isopropylidene-D-mannitol and a carbohydrate diol **3** were also cleaved to the corresponding aldehydes in reasonable yields. The ease of using NiO₂-Al₂O₃ in organic solvents for cleavage of diols indicates that this solid oxidizing agent may prove to be a useful alternative to sodium metaperiodate or lead tetraacetate.

Acknowledgement. This work was supported by a grant from Yonsei University.

References

- (a) M. Z. Barakat, M. F. Abdel-Wahab, and M. M. El-Sadr, *J. Chem. Soc.*, 4685 (1959); (b) L. Crombie and J. Crossley, *J. Chem. Soc.*, 4983 (1963); (c) I. T. Harrison, *Proc. Chem. Soc.*, 110 (1964).
- E. Santaniello and P. Ferraboschi, *Synth. Commun.*, **10**, 75 (1980).

- F. S. Guziec and F. A. Luzzio, *J. Org. Chem.*, **47**, 1787 (1982).
- K. S. Kim, Y. K. Chang, S. K. Bae, and C. S. Hahn, *Synthesis*, 866 (1984).
- K. S. Kim, S. J. Kim, Y. H. Song, and C. S. Hahn, *Synthesis*, 1017 (1987).
- K. S. Kim, S. Chung, I. H. Cho, and C. S. Hahn, *Tetrahedron Lett.*, **30**, 2559 (1989).
- M. V. George, in "Organic Syntheses by Oxidation with Metal Compounds", W. J. Mijs and C. R. H. I. De Jonge eds., Plenum Press, New York, pp. 373-422, (1986).
- K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).
- NiO₂ was prepared as described in reference 8.
- Al₂O₃ (W-200-B, Activity grade Super I) was purchased from ICN Pharmaceuticals, Inc. and used without further activation.
- The solid mixture was prepared by gentle grinding a mixture of NiO₂ and Al₂O₃ in a mortar for 2 min.
- M. Harfenist, A. Baviey, and W. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

Reaction and Coordination Chemistry of Ferrocenylphosphines with (η⁵-C₅H₅)Co(CO)₂-Crystal Structures of Two Ferrocenylphosphine Oxides

Tae-Jeong Kim*, Jung-Hee Lee, Soon-Chul Kwon, and Kee-Ha Kwon

*Department of Industrial Chemistry,
Kyungpook National University, Taegu 702-701*

Jae-Kook Uhm*, Hyuk Lee, and Sang-In Byun

*Department of Chemistry, Keimyung University,
Taegu 704-701*

Received February 11, 1990

There has been considerable interest in reactions catalyzed by ferrocenylphosphine derivatives of metals such as Rh, Ni, Pd, Pt, and Au¹⁻¹⁰. Of various chiral and achiral ferrocenylphosphine ligands those that have been most widely explored in connection with homogeneous catalysis are (η⁵-C₅H₄PPh₂)₂Fe(BPPF), (η⁵-C₅H₅)Fe(η⁵-C₅H₃(CHMeNMe₂)PPh₂-1,2)(PPFA), and (η⁵-C₅H₄PPh₂)Fe(η⁵-C₅H₃(CHMeNMe₂)PPh₂-1,2)(BPPFA). We have recently been interested in the synthesis of rhodium and iron complexes incorporating these ligands principally for use as catalyst precursors in the catalytic hydrogenation of polynuclear heteroaromatic compounds¹¹ and in the CO₂ activation for the synthesis of carbamates^{12,13}, respectively. During the course of our investigations we have noticed that the above ligands form a wide range of complexes with various coordination modes: a typical chelating bidentate, a monodentate diphosphine, or a bridging ligand in dimeric and trimeric species.