Tetrahedron Letters,Vol.24,No.23,pp 2399-2400,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

CERIUM(IV) AMMONIUM NITRATE-CHARCOAL SYSTEM. AN EFFECTIVE CATALYST FOR THE AIR OXIDATION OF BENZYL ALCOHOLS AND ACYLOINS

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Summary: Cerium(IV) ammonium nitrate (CAN) adsorbed on activated charcoal has been found to be an effective catalyst for the air oxidation of benzyl alcohols and acyloins to the corresponding carbonyl compounds.

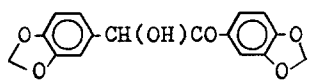
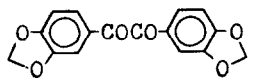
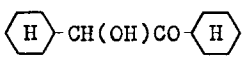
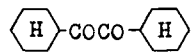
It is well known that, among various oxidants, tetravalent cerium compounds exhibit characteristic oxidizing ability.[1] Nevertheless, the practical use of these compounds as oxidizing reagents are limited to some special cases,[2-6] because the extremely strong oxidizing power of them often causes undesirable over-oxidations to result in complex reaction mixtures.[1] Only recently, a new method using a catalytic amount of cerium(IV) ion in the presence of sodium bromate was devised,[7,8] and it was successfully applied to the selective oxidation of alcohols.[9]

During the course of our investigation on the utilization of cerium and its major derivatives in organic synthesis,[10-12] we found that CAN adsorbed on charcoal effectively catalyzed the air oxidation of benzyl and related alcohols to afford the corresponding carbonyl compounds in good to high yields.[13] We wish to report herein some examples of this synthetically useful oxidation.

$$RR'CHOH \xrightarrow[(NH_4)_2Ce(NO_3)_6\text{-Charcoal}]{\text{Air}} RR'C{=}O$$

The preparation of the catalyst (CAN-Charcoal) and the subsequent air oxidation can be carried out conveniently. A typical experiment is as follows: Activated charcoal (Special Grade, purchased from Wako Pure Chemicals Ltd.) (3.00 g) was added to a solution of CAN (0.82 g) in water (100 ml) with stirring. After 10 min, the solid was collected by filtration and dried over P_2O_5 in vacuo for 15 h to give 3.85 g of catalyst. Next, a mixture of the catalyst (385 mg), which contained ca. 0.15 mmol of CAN, p-chlorobenzyl alcohol (1 mmol), and toluene (3 ml) was heated with stirring at 100 °C in an open flask. After 2 h, the reaction mixture was cooled and the catalyst was removed by filtration. The filtrate was concentrated and the residue was purified by preparative thin layer chromatography on silica gel to give p-chlorobenzaldehyde (117 mg, 82 %).

Table 1. Air Oxidation of Benzyl Alcohols and Acyloins Catalyzed by CAN-Charcoal

Entry[a]	Substrate	Catalyst (mol %)	Time (h)	Product	Yield[b] (%)
1	p-$ClC_6H_4CH_2OH$	15	2	p-ClC_6H_4CHO	82
2	p-$BrC_6H_4CH_2OH$	15	2	p-BrC_6H_4CHO	68
3	p-$O_2NC_6H_4CH_2OH$	15	1.5	p-$O_2NC_6H_4CHO$	78
4	p-$CH_3OC_6H_4CH_2OH$	15	2	p-$CH_3OC_6H_4CHO$	92
5[c]	$HO(CH_2)_3$-  -CH_2OH	20	16	$HO(CH_2)_3$--CHO	73
6	$C_6H_5CH(OH)COC_6H_5$	15	2	$C_6H_5COCOC_6H_5$	86
7	CH_3O-  -$CH(OH)CO$-  -OCH_3	15	18	CH_3O-  -$COCO$-  -OCH_3	92
8		15	20		86
9		20	9		82

a) All reactions were carried out in toluene at 100 °C unless otherwise stated.
b) Isolated yield. c) The reaction was performed in dioxane.

In a similar manner, various benzyl alcohols and acyloins were subjected to air oxidation.[14] The results are summarized in Table 1.

It is noted that the oxidation of benzyl alcohols afforded benzaldehydes without formation of benzoic acids. Another characteristic of this method is that, as is shown in Entry 5, benzylic alcohol moiety was selectively oxidized and other hydroxy group remained unaffected.

The oxidation of acyloins also proceeded cleanly to give α-diketones in high yields. The results are in sharp contrast to those obtained by the reaction using stoichiometric amount of CAN, in which C-C bond fission occurs to yield aldehydes and carboxylic acids.[15]

References and Notes 1) For a review, see: T-L. Ho, Synthesis, 1973, 354. 2) W. S. Trahanovsky, L. B. Young, and G. L. Brown, J. Org. Chem., 32, 3865 (1967). 3) G. Mehta, P.N. Pandy, and T-L. Ho, J. Org. Chem., 41,953 (1976). 4) L.Syper, K. Kloc, J. Mlochowski, and Z. Szulc, Synthesis, 1979, 521. 5) T. Uchimaru, K. Narasaka, and T. Mukaiyama, Chem. Lett., 1981, 1551. 6) K. Kamaike, H. Tsuchiya, and H. Takaku, Nucleic Acids Res. Sym. Series, 11, 69 (1982). 7) T-L. Ho, Synthesis, 1978, 936. 8) G. A. Olah, B. G. B. Gupta, and A. P. Fung, Synthesis, 1980, 897. 9) H. Tomioka, K. Oshima, and H. Nozaki, Tetrahedron Lett., 1982, 539. 10) T. Imamoto, Y. Hatanaka, Y. Tawarayama, and M. Yokoyama, Tetrahedron Lett., 1981, 4987. 11) T. Imamoto, T. Kusumoto, Y. Hatanaka, and M. Yokoyama, Tetrahedron Lett., 1982, 1353. 12) T. Imamoto, T. Kusumoto, and M. Yokoyama, Chem. Commun., 1982, 1042. 13) It was observed that CAN without adsorption on charcoal catalyzed the air oxidation of some benzyl alcohols in the presence of sulfuric acid or copper(II) chloride even though longer reaction time was required. 14) Under similar conditions, some ketoximes were also converted into the parent ketones. 15) T-L. Ho, Synthesis, 1972, 560.

(Received in Japan 7 March 1983)