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Oxidation of Aliphatic Secondary and Benzylic Alcohols to Carbonyl Compounds by Peracetic Acid in the Presence of Sodium Bromide in Acetic Acid

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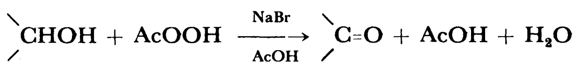
Synopsis. Alcohols were smoothly oxidized by peracetic acid in the presence of sodium bromide to give the corresponding carbonyl compounds in good yields.

The conversion of hydroxyl groups to the corresponding carbonyl groups is one of the most important methods for synthetic chemistry and many procedures have been developed. Many of them are the oxidation using metallic oxidants in amounts ranging from stoichiometric to large excess. However, these oxidants are environmentally hazardous and rather expensive. Thus, a number of catalytic systems including $[RuCl_2(PPh_3)_3]$-*t*-BuOOH,[1] pyridinium dichromate-$Me_3SiOOSiMe_3$,[2] $R_4N^+Br_4MoO^-$-*t*-BuOOH,[3] 2,4-dimethyl-2,4-pentanediol-CrO_3-peracetic acid,[4] and sodium bromate-hydrogen bromide[5] have recently been reported for this purpose. In this paper we report that aliphatic secondary and benzylic alcohols can be smoothly converted to carbonyl compounds in good yields by peracetic acid in the presence of sodium bromide.

Results and Discussion

The reaction of peracetic acid with alcohols was conducted in acetic acid in the presence of sodium bromide. GLC analysis showed that only carbonyl compound and starting material were involved in the product mixture under suitable conditions. Thus, a small excess of the oxidant was used for the completion of the reaction. The results were summarized in Table 1.



$$\rangle CHOH + AcOOH \xrightarrow[AcOH]{NaBr} \rangle C{=}O + AcOH + H_2O$$

Benzylic and aliphatic secondary alcohols (Entries 1—8) were converted smoothly to the corresponding carbonyl compounds in good yields by using 10—20% excess of peracetic acid and 0.5—1 equivalent of sodium bromide. The oxidation of hindered aliphatic secondary alcohols was slow and thus the oxidation of terpenoid alcohols (Entries 9—11) required 1.5 equivalent of sodium bromide as promoter and 50% excess of peracetic acid as an oxidant in order to get good yields of the products. Aliphatic primary alcohols were much slowly oxidized to give aldehydes in poor yields. The oxidation in raised temperature was unsuccessful, perhaps due to the self-decomposition of peracetic acid.

In order to clarify a real active species and reaction path of the present reaction, the independent oxidations of benzyl alcohol with peracetic acid, with bromine and also with the combination of these two reagents were carried out, since peracetic acid is a strong oxidant and bromine, which may be formed during the reaction, is also an oxidant. Peracetic acid, itself, could not oxidize the alcohol to benzaldehyde but converted it to benzyl acetate in the absence of sodium bromide. Indeed bromine itself also oxidized the alcohol, but the reaction was considerably slow and resulted in lower yield of benzaldehyde. The combination of peracetic acid with bromine gave the better results (60—70% yield by GLC analysis) but the

Table 1. The Oxidation of Alcohols by Peracetic Acid-Sodium Bromide in Acetic Acid

Entry No.	Alcohol[a]	AcOOH/Sub. mole ratio	NaBr/Sub. mole ratio	Temp °C	Time h	Yield[b] mol%
1	$PhCH_2OH$	1.1	1.0	60	2	91
2	$PhCH(OH)CH_3$	1.1	0.1	60	2	86
3	$Ph_2CH(OH)$	1.1	0.5	60	2	75
4	2-Heptanol	1.2	0.5	30	1	79
5	2-Octanol	1.1	0.5	30	1	81
6	2-Methylcyclohexanol	1.2	0.7	30	1	89
7	4-*t*-Butylcyclohexanol	1.2	1.0	30	1	88
8	Cyclododecanol	1.2	0.7	40	1	93
9	*l*-Menthol	1.5	1.5	60	2	91
10	Borneol	1.5	1.5	30	2	88
11	Isoborneol	1.5	1.5	30	2	94

a) Ca. 0.5 g of substrates were used in every run. b) Isolated yields.

yield was inferior to those by the combination of peracetic acid and sodium bromide. These results may show that the true oxidant for alcohol is acetyl hypobromite which comes from the reaction of peracetic acid with bromide ion or bromine. Acetyl hypobromite has been suggested to be a reacting species for the bromination[6] of aromatic compounds and bromoacetoxylation[7] of olefins by peracetic acid–bromine or bromide ion. Thus, the acetyl hypobromite might be a real active oxidant.

$$\mathrm{AcOOH + AcOH + NaBr \longrightarrow AcOBr + AcONa + H_2O}$$

$$\mathrm{AcOBr} + \mathrm{\rangle CHOH} \longrightarrow \mathrm{AcOH + HBr} + \mathrm{\rangle C{=}O}$$

$$\mathrm{AcONa + HBr \longrightarrow AcOH + NaBr}$$

The present reaction may be a useful process of synthesizing simple ketones from the economical and environmental points of view, since the reagents used are cheap, the yields are good and nothing except water and acetic acid is formed.

Experimental

^{1}H NMR spectra were measured for solutions in CCl_4 on a JEOL model PMX-60 spectrometer. IR spectra were recorded for thin film or KBr disk on a JASCO DS-403G spectrophotometer. GLC was carried out on a Shimadzu GC-6A instrument with a 2-m glass column packed with 5% PEG-20M on Chromosorb WAW-DMCS or on a Shimadzu GC-4C instrument with a 2-m glass column packed with 1.5% Silicone OV-17 on Chromosorb WAW-DMCS, with temperature programming.

All reagents were commercially available and were used without purification. Peracetic acid was prepared from 60% hydrogen peroxide and acetic anhydride[7] and the concentration was determined by the iodometry.

Oxidation Procedures. A typical procedure is as follows. Sodium bromide (ca. 0.5 g), alcohol (0.5 g), and acetic acid (3 ml) were placed in a two naked round-bottomed flask, equipped with a dropping funnel and a condenser, the top of which was connected to the argon-filled balloon. After flashing with argon, peracetic acid (2—3 mol dm^{-3}) was added dropwise to the magnetically stirred mixture for a given period and the stirring was continued for an another hour. The reaction mixture was poured into brine (30 ml) and the product was extracted with ether (15 ml×3). Combined ethereal solution was washed with brine, 10% aq Na_2CO_3, and brine and then dried (Na_2SO_4). After filtration, the ether was removed on a rotary evaporator under a reduced pressure to give colorless to pale-yellow oil or solid, which was purified by flash chromatography (silica GLC and hexane–ethyl acetate). Products were identified by ^{1}H NMR and IR spectra. GLC analyses showed that the purities of products were satisfactory.

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