Oxidation of Alcohols to Carbonyl Compounds with Peracetic Acid catalysed by Cobalt(III) Acetate

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Some alcohols have been oxidized to carbonyl compounds with peracetic acid catalysed by cobalt(III) acetate in acetic acid. The addition of sodium bromide to the reaction mixture accelerated the reaction. The oxidation of primary and secondary aromatic alcohols with peracetic acid catalysed by cobalt acetate and sodium bromide gave, respectively, the corresponding aldehydes and ketones in excellent yields. Secondary aliphatic and alicyclic alcohols were converted into the corresponding ketones in moderate to good yields under similar conditions, but primary aliphatic alcohols did not react.

Cobalt(III) acetate is commercially used as a catalyst for the autoxidation of polymethylbenzenes and aldehydes to the corresponding carboxylic acids and cyclohexane to cyclohexanone.[1,2] Initiation is considered to involve hydrogen abstraction from the hydrocarbon by cobalt(III) acetate. Indeed, there are many reports that cobalt(III) acetate can oxidize organic compounds in acetic acid under nitrogen.[1-3] In autoxidizing conditions, cobalt(III) acetate can be regenerated by the reaction of cobalt(II) acetate with hydroperoxide formed during the reaction [equation (1)].

$$\mathrm{Co^{II} + ROOH \longrightarrow Co^{III} + RO^{\bullet} + OH^-} \quad (1)$$

Therefore, if a previously prepared hydroperoxide is used for the oxidation of cobalt(II) acetate formed during the reaction, oxidation by the combination of these two reagents may be equivalent to stoicheiometric oxidation by cobalt(III) acetate. Peracetic acid was selected as oxidant, since it is reported that cobalt(III) acetate can be prepared by the oxidation of cobalt(II) acetate with peracetic acid in acetic acid.[4] The method has some merits in that the reaction can be carried out under nitrogen and also commercial cobalt(II) acetate may be used instead of previously prepared cobalt(III) acetate.

In this paper, we report the oxidation of various alcohols to the corresponding carbonyl compounds with peracetic acid catalysed by cobalt acetate under nitrogen. Similar catalytic systems have been developed for the effective use of metal ions such as Os, Mo, Pd, W, Ce, Mn, *etc.* for the oxidation of various organic compounds including alcohols.[1]

Results and Discussion

Peracetic acid was added dropwise through a dropping funnel to a stirred mixture of benzyl alcohol and cobalt(II) acetate in acetic acid under nitrogen. As soon as a drop of peracetic acid was added to the reaction mixture, the colour of the solution changed from pink to dark green which then gradually returned to the original colour, showing that the cobalt(III) acetate was formed and the species was then reduced by the alcohol.

In the absence of cobalt(II) or cobalt(III) acetate, addition of peracetic acid to benzyl alcohol in acetic acid gave almost quantitatively benzyl acetate and no benzaldehyde was detected. In the absence of peracid, esterification is much slower and only 10—20% of ester can be obtained under similar conditions. It is not clear why benzyl acetate forms so easily under these conditions.† In contrast, the presence of 10 mole % of cobalt(II) acetate gave benzaldehyde together with a small amount of benzyl acetate which was formed always in trace amount under these conditions. These facts may show that the real oxidant is cobalt(III) acetate [equation (3)] but not peroxide in this system and peroxide only generates the oxidant from cobalt(II) acetate added initially and/or formed during the reaction [equation (2)]. Thus, the net reaction may be illustrated by equation (4).

$$\mathrm{PhCH_2OH + 2\,CO^{III} \longrightarrow PhCHO + 2\,H^+ + 2\,Co^{II}} \quad (2)$$

$$\mathrm{2\,Co^{II} + AcOOH \longrightarrow 2\,Co^{III} + AcOH + [O^{2-}]} \quad (3)$$

$$\mathrm{PhCH_2OH + AcOOH \longrightarrow PhCHO + AcOH + H_2O} \quad (4)$$

The results of the oxidation of benzyl alcohol with peracetic acid in the presence of catalytic amounts of cobalt(II) acetate are listed in Table 1 together with that in the absence of cobalt(II) ion. When benzyl alcohol with more than three equivalents of peracetic acid was used, benzaldehyde was obtained in high yield on the basis of added peracid but an increase in the amount of peracetic acid decreased the yield of the aldehyde. This decrease in yield may be partly due to slow oxidation of the alcohol by cobalt(III) acetate and thus a considerable amount of peracetic acid may be consumed only by the unproductive self-decomposition.

If the reaction between the alcohol and cobalt(III) acetate could be accelerated and the concentration of cobalt(II) ion in the reaction mixture increased, then the yield of the aldehyde should increase since the ratio of peracetic acid available for the oxidation of cobalt(II) ion would be increased. Thus, we

Table 1. Oxidation of benzyl alcohol with peracetic acid catalysed by cobalt(III) acetate.

$PhCH_2OH$ (mmol)	AcOOH (mmol)	$Co(OAc)_2$ (mmol)	Temp. (°C)	Time (h)	PhCHO[a] (%)
20	20	1	80	2	40.8
20	10	1	90	2	68.9
20	6.4	1	80	2	98.4
20	20	0	80	1	97.1[b]

[a] G.l.c. yield. [b] Yield of benzyl acetate.

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† Esterification under the same conditions is limited to aromatic alcohols and aliphatic alcohols were not esterified by peracid in acetic acid.

Table 2. Effects of additives on the yields of benzaldehyde

$PhCH_2OH$ (mmol)	AcOOH (mmol)	$Co(OAc)_2$ (mmol)	Additives (mmol)	Temp. (°C)	Time (h)	PhCHO (%)
20	9.7	1	TFA (5.4)	90	2	23.6 (64.5[a])
20	9.7	1	MEK (1.3)	90	2	75.0
20	10.2	1	NaBr (1.0)	90	2	100.5
20	9.7	1	NaBr (1.0)	90	2	100.4
12	10.0	1	NaBr (2.0)	60	1	100.1
10	9.9	1	NaBr (2.0)	60	1	96.7

TFA = CF_3COOH, MEK = butan-2-one. [a] Yield of benzyl acetate.

Table 3. Oxidation of substituted benzyl alcohols

Substituent (mmol)		AcOOH (mmol)	$Co(OAc)_2$ (mmol)	NaBr (mmol)	Temp. (°C)	Time (h)	Yield (%)
p-CH_3O	(8.48)	7.0	0.7	4.3	50	2	80.2
	(11.3)	11.3	1.0	5.0	50	1	74.2
p-CH_3	(10.9)	9.1	0.9	2.0	40	1	84.1
	(11.3)	11.3	1.0	5.0	60	1	72.1
p-Cl	(10.3)	8.5	0.9	5.0	60	2	95.7
p-NO_2	(10.3)	8.5	1.0	5.0	60	2	55.0[a]
$PhCH(OH)CH_3$	(10.3)	8.6	0.8	0.8	60	1	100
	(8.48)	8.4	0.9	0.9	60	1	96.0
$Ph_2CH(OH)$	(6.62)	8.4	0.8	0.1	60	1	99.0[a]
	(8.40)	8.4	0.8	0.8	60	1	97.5[a]
PhC(=O)CH(OH)Ph	(5.85)	6.7	0.6	2.3	60	1	96.3

[a] Isolated yield.

examined the effect of butan-2-one and trifluoroacetic acid which were used as promoters of cobalt-catalysed autoxidation of cobalt(III) acetate oxidation of organic compounds, respectively.[5-8] The addition of trifluoroacetic acid accelerated the reaction but benzyl acetate was mainly obtained and the yield of benzaldehyde decreased. The addition of butan-2-one slightly increased the yield. In contrast, the addition of bromide ion, which was well known as a promoter of autoxidation catalysed by cobalt acetate,[1,2] accelerated the reaction and also drastically increased the yield of benzaldehyde. When an excess of alcohol was used, a quantitative yield of benzaldehyde was obtained as shown in Table 2. The result demonstrates that all the peroxide was consumed in the conversion of alcohol into aldehyde. The use of the equal quantities of peroxide and alcohol still gave an excellent yield but excess of oxidant resulted in a decreased yield of benzaldehyde, perhaps due to the further oxidation of the aldehyde. In the absence of cobalt acetate, the alcohol was oxidized to aldehyde in 50—60% yield by peracetic acid and sodium bromide in acetic acid, but a considerable amount of benzyl acetate was obtained together with the aldehyde. Hence, the presence of cobalt and bromide ions is necessary for the effective use of peracetic acid.

Various aromatic alcohols were oxidized to the corresponding aldehydes or ketones with peracetic acid catalysed by the Co–Br system (Table 3). All aromatic alcohols tried in the present work were converted into the corresponding aldehydes in good to excellent yields. In the oxidation of primary aromatic alcohols, an equal or excess quantity of sodium bromide over cobalt acetate was necessary for effective oxidation and a moderate rate. However, secondary aromatic alcohols could be oxidized to the corresponding ketones in excellent yield by using cobalt(III) acetate and a smaller amount of sodium bromide.

The results of the oxidations of aliphatic and alicyclic alcohols with the same oxidant are summarized in Table 4. Secondary aliphatic alcohols were oxidized by the system to give ketones in moderate to good yields by using a considerable excess of sodium bromide to cobalt acetate although the reaction was slower under the conditions used for aromatic alcohols. Similar results were obtained for the oxidation of alicyclic compounds, except for that of 2-methylcyclohexanol. The low yield of 2-methylcyclohexanone may be due to its further reaction since it is found by a separate experiment that the ketone is easily brominated by cobalt(III) acetate and sodium bromide in acetic acid.[9] On the other hand, primary alcohols were not oxidized by the oxidant and almost all substrates were recovered unchanged. For example, the oxidation of octan-1-ol, heptan-1-ol, and 2-phenylethanol gave the corresponding aldehydes in only 1—3% yield under the conditions shown in Table 4 for the oxidation of secondary aliphatic compounds. There were no effects of increasing sodium bromide concentration on the yields of aliphatic aldehydes.

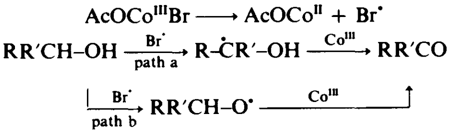
The order of reactivities of alcohols with the oxidant seems to show that a radical species is involved as an intermediate. In the autoxidation of hydrocarbons catalysed by the Co–Br system, the active species is considered to be a 1 : 1 complex of cobalt and bromide ion.[10] The complex decomposes to liberate a bromine atom which can abstract a hydrogen atom to initiate a radical chain reaction. On the basis of this mechanism, it may be suggested that the present reaction proceeds with a hydrogen abstraction from alcohol by bromine atom to give a radical followed by the oxidation with cobalt(III) acetate.

When hydrogen is abstracted from a hydroxy group, all alcohols may be oxidized with similar rates because the stabilities and reactivities of the hydroxyl radicals are not seriously different from each other. Thus, path b may be ruled out. This is supported by the fact that the bond dissociation energy of the O–H bond (*ca.* 110 kcal mol^{-1}) is higher than those of the C–H bonds (<100 kcal mol^{-1}).[11] A bromine atom abstracts an α-hydrogen from alcohol to give a carbon radical. The stability of radicals generally increases in the order primary $<$ secondary $<$ tertiary, and benzylic radicals are much more

Table 4. Oxidation of aliphatic and alicyclic alcohols at 60 °C

Alcohol (mmol)	AcOOH (mmol)	$Co(OAc)_2$ (mmol)	NaBr (mmol)	Time (h)	Conversion (%)	Yield[a] (%)
Heptan-2-ol (6.51)	8.20	0.65	2.7	1	96.8	67.3
Octan-2-ol (6.89)	8.20	0.76	2.8	1	92.3	82.7
Cyclohexanol (10.7)	8.60	0.86	5.16	2	68.5	45.7
2-Methylcyclohexanol (6.51)	7.68	0.65	2.67	1	63.1	17.3
3-Methylcyclohexanol (5.92)	7.00	0.59	2.90	0.5	79.0	73.5
4-t-Butylcyclohexanol (5.18)	7.67	0.52	2.02	1	82.9	69.1[b]
Cyclododecanol (6.79)	8.15	0.68	2.72	1	89.8	67.4

[a] Based on consumed alcohol. [b] 40 °C.



Scheme.

stable. There is no doubt that the order of reactivities of the present reaction is parallel to the stabilities of the radical intermediates.

It is well known that the bromine atom has good selectivity and low reactivity.[12] Hence, aromatic alcohols can be easily oxidized, and secondary aliphatic and alicyclic alcohols can be converted less easily. However, primary alcohols did not react because of the instability of the intermediate radical or the low reactivity of bromine atom.

There are many reports on the oxidation of alcohols to carbonyl compounds, and benzyl alcohols can be smoothly converted into benzaldehydes with many oxidants.[13] However, stoicheiometric or excessive amounts of oxidant are used in these reactions. Recently, from the economic and environmental points of view, metal-catalysed oxidations of alcohols with various oxidants have been developed[14–16] but expensive metallic salts are used as catalysts. The present reaction is also a catalytic system for the oxidation of alcohols and catalysts, cobalt acetate and sodium bromide are much cheaper reagents than those used in the literature. Hence, the present reaction is useful for preparing benzaldehydes from benzyl alcohols. This system can also be applied to the oxidation of aliphatic and alicyclic alcohols.

Experimental

Gas chromatography was carried out on a Shimazdu GC-6A instrument with a 2 m glass column packed with 5% PEG-20M on Chromosorb GAW-DMCS, with temperature programming. For measurements of yields, an internal standard was used.

All reagents were commercially available and were used without further purification. Peracetic acid was prepared from acetic anhydride and hydrogen peroxide. Its concentration was determined iodometrically.

Oxidation Procedure.—A typical procedure is as follows. In a three-necked flask equipped with a condenser and a dropping funnel, peracetic acid was added dropwise to the mixture of cobalt(II) acetate and alcohol in acetic acid stirred with a magnetic stirrer under nitrogen. After complete addition of the peroxide, the solution was stirred for another 1 h. After the addition of the internal standard, the reaction mixture was poured into water and the products were extracted with ether. The extract was successively washed with aqueous Na_2CO_3 and water and then dried (Na_2SO_4). Evaporation of the ether left an oil which was analysed by g.l.c. under the conditions described above. The yields of products were corrected by a calibration curve which was made for every product.

Acknowledgements

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