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Oxidation of Benzylic and Allylic Alcohols with Cobalt(III) Acetate in Acetic Acid in the Presence and Absence of Sodium Bromide

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Synopsis. Benzyl alcohol and its *o*-, *m*-, and *p*-substituted derivatives afforded fairly good yields of the corresponding benzaldehydes through a reaction with a Co(III)-NaBr system. With allylic alcohols, this system failed in a selective formation of unsaturated carbonyl compounds. In the latter cases, the products were effectively obtained by using a higher concentration of cobalt(III) acetate in the absence of NaBr.

Cobalt(III) acetate is a potent oxidant; on kinetic grounds,[1,2] the oxidation of organic compounds with it has been considered via an electron-transfer mechanism. Compared with other metal oxidants such as Pb(IV), Tl(III), Hg(II), Cr(VI), Se(IV) salts etc., some advantages in terms of relatively low cost, simple manipulation and, especially lower toxicity of cobalt(III) acetate make it considerably attractive in the oxidation of various olefins.[3-5] The present paper describes the oxidation of benzylic and allylic alcohols with cobalt(III) acetate in acetic acid since, hitherto, there has only been little data on this subject. In addition, the effect of added sodium bromide on the reaction rate as well as on the product yield is reported.

Results and Discussion

The oxidation of benzyl alcohol (**1**) in acetic acid with a stoichiometric amount (2 equiv. per mole of **1**) of cobalt(III) acetate was conducted under an inert atmosphere (argon) since the main product, benzaldehyde (**2**), is highly susceptible to autoxidation. After heating the reaction mixture at 60 °C for 2 h, it was observed that cobalt(III) acetate was not completely consumed, as judged from the dark-green color of the solution. A GLC analysis revealed that **1**, **2**, and a minor amount (GLC selectivity; 4.2%) of benzyl acetate (**3**) was involved in the product mixture. Then, the reaction was carried out in the presence of NaBr, known as a promoter in cobalt-catalyzed autoxidation of alkylbenzenes.[6,7] In this case, the initially dark-green solution became blue-black as the NaBr gradually disappeared. When the reaction mixture was poured into brine, the aqueous layer became cobaltous pink, suggesting that almost all the cobalt(III) acetate had been consumed. Indeed, the conversion of **1** was considerably increased upon the addition of a small amount of NaBr (Table 1), whereas **3** decreased to a trace amount. These observations imply that NaBr contributes not only to accelerate the reaction, but to inhibit any side-reaction. The yield of **2** gradually increased upon increasing the amount of NaBr and reached a maximum at NaBr/**1**=0.5. However, a further addition of NaBr no longer contributed to the formation of **2**.

The oxidation of substituted benzyl alcohols was performed in a manner similar to that of **1**, resulting in a predominant formation of the corresponding benzaldehydes. Compared with the other substrates, the oxidation of nitrobenzyl alcohols did not proceed so readily in the absence of NaBr, viz. the conversion of *p*-nitrobenzyl alcohol (**4**) was 65% at 60 °C for 2 h. On the other hand, *p*-methoxybenzyl alcohol (**5**) showed a higher reactivity. Thus, 77% of **5** was converted under comparable conditions.

As with the case of **1**, an addition of NaBr usually accelerated the oxidation of substituted benzyl alcohols, leading to a selective formation of the corresponding benzaldehydes. Indeed, the conversion of **4** increased to 97% upon the addition of NaBr(NaBr/**4**=

Table 1. Oxidation of Benzyl Alcohol in the Presence and Absence of Sodium Bromide[a)]

NaBr/Sub. mole ratio	Recovered alcohol[b)]	Yield of benzaldehyde[b)]
0	21	75
0.1	7.3	81
0.3	4.4	83
0.5	4.2	89
0.7	4.9	83
1.0	4.2	76

a) Under argon, 60 °C, 2 h; ca. 0.5 g of substrate and a stoichiometric cobalt(III) acetate were used in every run. b) GLC yield in mol%.

Table 2. Oxidation of Benzyl Alcohols[a)]

		Time	Temp	NaBr/Sub	Benzaldehyde[b)]
		h	°C	mole ratio	%
H		2	60	0.5	86
Me	*o*-	2	50	0.5	75
	m-	2	50	0.5	91
	p-	2	60	0.5	81
OMe	*o*-	2.5	50	0.1	87
	m-	2	50	0.5	87
	p-	4	60	0.5	88
Br	*o*-	2	70	0.5	87
	m-	2	70	0.5	88
	p-	2	60	0.5	92
Cl	*o*-	2	70	0.5	91
	m-	2	70	0.5	91
	p-	4	60	0.1	85
NO_2	*o*-	2	70	0.5	72
	m-	2	70	0.5	83
	p-	2	60	0.5	82

a) Under argon; ca. 0.5 g of substrates and a stoichiometric cobalt(III) acetate were used in every run. b) Isolated yield.

Table 3. Oxidation of Allylic Alcohols[a)]

	Time h	Temp °C	Co(III)/Sub. mole ratio	Product[b)] Yield/%
Cinnamyl alcohol	4	60	2.5	Cinnamaldehyde 62
Geraniol	24	40	2.5	Citral 63
1-Octen-3-ol	6	60	3.0	1-Octen-3-on 72
trans-2-Hexen-1-ol	6	60	5.0	*trans*-2-Hexenal 71

a) Under argon; ca. 0.5 g of substrates were used in every run. b) Isolated yield.

0.5) under the same conditions as mentioned above. The results of various substituted benzyl alcohols are summarized in Table 2. The reaction conditions (temperature, time, and concentration of NaBr) were determined on the basis of the reactivity of the substrates as well as the yield of the aldehydes. In all cases, GLC analyses showed that no neutral product, other than the aldehydes, was formed in a significant amount under the conditions employed. As shown in Table 2, substituted benzaldehydes were obtained in excellent yields, irrespective of the nature of the substituents or of the position of those on the benzene-ring. Consequently, the present procedure was proved to be applicable to a wide variety of substituted benzyl alcohols.

The reaction of allylic alcohol was also promoted upon the addition of NaBr. For example, conversions of 1-octen-3-ol in reactions with a stoichiometric amount of cobalt(III) acetate at 60 °C for 2 h were 26, 63, 70, and 77% when the mole ratios of NaBr/substrate were 0, 0.1, 0.5, and 1.0, respectively; at this time the GLC selectivities of the main product, 1-octen-3-on (**6**), were 24, 49, 52, and 50%, respectively. However, the unknown products increased and, thus, the selectivity of **6** decreased in proportion to the amount of NaBr added. The failure of a selective formation of **6** in the presence of NaBr might be explained by the facts that an olefinic double bond has been suggested to be as susceptible to cobalt(III) acetate as hydroxyl group[2)] and that cobalt(III)–NaBr system is an effective reagent for allylic oxidation.[8)] A close inspection of the reaction conditions revealed that a reaction with an excess amount of cobalt(III) acetate in the absence of NaBr for a relatively long time is appropriate for an effective formation of unsaturated carbonyl compounds from allylic alcohols (Table 3).

In connection with the initial stage of the reaction, cobalt monobromide has been suggested as being an active species in the autoxidation of hydrocarbons catalyzed by cobalt(II) acetate in the presence of NaBr.[6)] However, an intervention of the bromine radical cannot be ruled out, since any product study regarding the oxidation of alicyclic olefins with a cobalt(III)–NaBr system can be rationally interpreted in terms of a participation of the bromine radical.[8)] The specification of an active species is now under way in our laboratory.

The present reaction requires stoichiometric or higher amounts of cobalt(III) acetate and is of limited utility for large-scale oxidation. However, the oxidation of benzylic alcohols with a cobalt(III) acetate–NaBr system offers a conventional method for synthesizing benzaldehydes, since products can be selectively obtained within a reasonable period of time, regardless of nature or the position of the substituents on the benzene-ring.

Experimental

^{1}H NMR spectra were obtained with a JEOL model PMX-60 spectrometer for solutions in carbon tetrachloride. IR spectra were recorded for thin films or KBr disks on a JASCO DS-403G spectrophotometer. GLC was carried out on a Shimadzu GC-6A or GC-4CM instrument with a 2 m column packed with 5% PEG-20M or 1.5% OV-17, respectively, on Chromosorb WAW-DMCS.

Materials. All alcohols were commercially available and were purified by conventional procedures just before use. Cobalt(III) acetate in acetic acid was prepared according to method described in the literature;[9)] the concentration was determined by Fe(II) and back titration with Ce(IV).

Oxidation Procedures. The following procedures are representative. To a mixture of benzyl alcohol (ca. 0.5 g) and NaBr (0.5 mol equiv) in a round-bottomed flask was added cobalt(III) acetate in acetic acid (2 mol equiv); the flask was then flushed with argon. The reaction was carried out at a controlled temperature in a thermostat with magnetic agitation. After a given period, the reaction mixture was poured into brine and extracted three times with ether. The combined extract was successively washed with brine, 10% aqueous sodium carbonate, and brine and then dried (Na_2SO_4). Removing the ether on a rotary evaporator yielded a light-yellow oil, which was chromatographed on silica gel (hexane–AcOEt).

All products, so obtained, were known compounds and were identified by comparisons of their NMR and IR spectra with those of authentic samples.

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