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Oxidation of Aromatic *s*-Alcohols with Cobalt(III) Acetate in the Presence of Sodium Bromide

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Synopsis. The title oxidation in acetic acid resulted in a selective formation of the corresponding ketones in excellent yields under mild conditions.

Oxidative transformation of alcohols to the corresponding carbonyl compounds constitutes an important part of synthetic chemistry. Thus, a wide variety of metal oxidants have been used for the stoichiometric and/or catalytic oxidation of alcohols. Extensively studied examples are those with lead(IV) acetate,1) chromium(VI) compounds,2—4) active manganese(IV) dioxide,5—7) aluminum alkoxides (Oppenauer oxidation),8) potassium ferrate(IV),9) cerium(IV) ammonium nitrate,10) etc. In economical and environmental terms, however, these procedures are not entirely satisfactory, because of the inherently hazardous toxicity and rather high cost of the reagents. In addition, from an experimental point of view, some limitations, viz. a lack of generality, manipulative complications, low yield of the product etc., have reduced the utility of the reagents for this purpose.

Cobalt salts are potent reagents and have wide applications for the oxidation of various functional groups, especially for the oxidation of alkylaromatics11—13) and olefins.14—16) However, there has hitherto been only a small amount of data on the oxidation of alcohols,17,18) and it is apparent that these are not adequate for estimating the full validity of the reagent for this objective. We have found that cobalt(III) acetate in acetic acid is an efficient reagent for the oxidation of 1,2-glycols;19—21) this fact prompted us to examine the oxidation of a variety of alcohols. The present paper describes the oxidation of aromatic *s*-alcohols using a cobalt(III) acetate–NaBr system, since this procedure can be expected to overcome the drawbacks attendant on conventional methods.

Results and Discussion

Oxidation of 1-phenylethyl alcohol (**1**) in acetic acid with stoichiometric cobalt(III) acetate [2 equiv per mol of **1**] was performed under an inert atmosphere in order to exclude any influence of autoxidation, since an alcohol has a rather high sensitivity to cobalt(III)-catalyzed autoxidation.17) After heating the reaction mixture at 60 °C for 2 h in the absence of NaBr, a GLC analysis showed that a considerable amount of unreacted **1** (38%) and only 49% of acetophenone (**2**), along with ca. 7% of 1-phenylethyl acetate (**3**) were involved in the reaction mixture. Upon the addition of a small amount of NaBr ([NaBr]/[Co(III)]=0.05; mole ratio), the conversion of **1** was markedly increased to roughly 94%, whereas **3** decreased to a trace amount. Consequently, NaBr contributes not only to facilitate the reaction, but to inhibit any side reaction. The yield of **2** was independent of the concentration of NaBr in the range [NaBr]/[Co(III)]=0.05—0.5.

Various inorganic bromides (KBr, LiBr, and $MgBr_2$) were also examined. All of the bromides were effective, and there was no marked difference in efficacy between NaBr and them. Thus, subsequent reactions were carried out using NaBr, since the reagent is inexpensive and easy to handle, as compared with the other bromides.

The oxidation of 1-phenylethyl alcohols and diarylmethanols was conducted under comparable conditions and the results are summarized in Table 1. As with the case of **1**, the addition of NaBr commonly resulted in the promotion of the reaction and also in the predominant formation of the corresponding ketones. When the oxidation was carried out with stoichiometric cobalt(III) acetate, the formation of a small amount of the corresponding acetate, possibly due to competitive acetylation of unreacted alcohol, was observed in some cases. Therefore, the experiments were performed with a small excess of the oxidant for the completion of the reaction in such cases. Depending on the conditions used, a concomitant formation of some unidentified by-products was also observed in the oxidation of phenyl-*o*-, -*m*-, and -*p*-tolylmethanol and *o*-methyldiphenylmethanol. This might be partly attributable to the susceptibility of the methyl side chain towards cobalt(III) acetate11,12) and/or the Co(III)–NaBr system.13) Thus, the other reaction conditions (temperature, time, and concentration of NaBr) were selected on the basis of the reactivity of alcohol as well as the yield and selectivity of the ketone.

The influence of the position of the substituents on the benzene-ring on the yield of the ketones was investigated (Entries 2—4, 6—8, 9—11, 15—17, and 20—22); interestingly, however, there was no significant difference in the yields of the ketones.

In order to clarify an active species, the independent oxidations of **1** and diphenylmethanol with bromine were carried out in acetic acid under comparable conditions (60 °C, 2 h), since bromine might be formed by the possible interaction of bromide ion with cobalt(III) acetate. Indeed, bromine itself can oxidize the alcohols, but afforded only lower yields of **2** and benzophenone (23 and 18%, respectively). In these reactions acetylation of the alcohols (65 and 64%, respectively) was predominant, showing little contribution of bromine in the present reaction. Moreover, when cobalt(III) acetate was heated without the addition of a substrate under "standard conditions" (60 °C

Table 1. Oxidation of Aromatic *s*-Alcohols with Cobalt(III) Acetate in the Presence of Sodium Bromide[a]

$$X\text{-}C_6H_4\text{-}CH(OH)\text{-}R \longrightarrow X\text{-}C_6H_4\text{-}C(=O)\text{-}R$$

Entry No.	Alcohols			Temp	Time	NaBr[b]	Co(III)[b]	Ketones[c]
	X		R	°C	h	Co(III)	Sub	%
1	H		Me	60	2	0.05	2.0	91
2	Me	*o*-	Me	50	2	0.05	2.5	84
3		*m*-	Me	50	2	0.05	2.5	97
4		*p*-	Me	50	2	0.05	2.2	86
5	OMe	*p*-	Me	60	2	0.25	2.2	96
6	Br	*o*-	Me	60	1.5	0.05	2.5	93
7		*m*-	Me	60	1.5	0.05	2.5	96
8		*p*-	Me	60	2	0.25	2.2	90
9	Cl	*o*-	Me	60	1	0.05	2.5	96
10		*m*-	Me	60	2	0.05	2.5	95
11		*p*-	Me	60	2	0.25	2.2	93
12	F	*p*-	Me	60	2	0.25	2.2	90
13	NO_2	*p*-	Me	70	2	0.25	2.2	84
14	H		Ph	60	2	0.25	2.0	94
15	Me	*o*-	Ph	60	2	0.05	2.5	92
16		*m*-	Ph	60	1	0.05	2.5	95
17		*p*-	Ph	60	1	0.05	2.0	93
18	OMe	*p*-	Ph	60	1.5	0.05	2.5	97
19	Br	*p*-	Ph	60	1.5	0.25	2.5	93
20	Cl	*o*-	Ph	60	1	0.05	2.5	93
21		*m*-	Ph	60	1	0.05	2.5	96
22		*p*-	Ph	60	2	0.25	2.0	91
23	NO_2	*p*-	Ph	70	2	0.05	2.5	93
24	Benzoin			60	2	0.25	2.0	83

a) Under argon, $[Co(OAc)_3]=0.2703\ mol\,dm^{-3}$; 0.50 g of alcohols were used in every run. b) Mole ratio. c) Isolated yield.

for 2 h) in both the presence and absence of NaBr ($[NaBr]/[Co(III)]=0$, 0.15, 0.25, 0.35, and 0.5), we observed that the concentration of a cobaltic species remained essentially unchanged within the experimental error; the ratios of concentration of remained Co(III) vs. initial concentration of Co(III) were 1, 0.995, 0.974, 0.989, and 0.979, respectively. Based on these observations and on earlier studies,[13,22] the reacting species is thought to be acetoxybromocobalt(III), formed from a reaction of cobalt(III) acetate with bromide ion. The species, so generated, is presumed as a highly active mononuclear complex.[23] Its

$$Co(OAc)_3 + Br^- \rightarrow (AcO)_2CoBr + AcO^-$$

highly reactive nature is very consistent with the marked rate enhancement observed in the present reactions. The cobaltic species could abstract the α-hydrogen atom of an alcohol in a radical manner,[22] finally giving the corresponding ketone by the following oxidation of the resultant carbon radical with cobalt(III) acetate.

Experimental

^{1}H NMR spectra were measured 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 GAW-DMCS, with temperature programming.

Materials. Cobalt(III) acetate in acetic acid was prepared according to lit.[24] The concentration was determined by adding an excess of Fe(II) and back-titration with Ce(IV) ion. 1-Phenylethyl alcohol, diphenylmethanol, phenyl-*o*-tolylmethanol and phenyl-*p*-tolylmethanol, *p*-chlorophenyl-phenylmethanol, and benzoin were commercially available. The other alcohols were synthesized by reductions of the corresponding ketones, either with $NaBH_4$ in 90% aqueous EtOH, with $LiAlH_4$ in dry ether, or with aluminum isopropoxide in 2-propanol. All of the alcohols, thus prepared, were purified by distillation or by recrystallization just before use. The commercial inorganic bromides were used without any treatment.

Oxidation Procedures. The following procedures are representative. To a mixture of **1** (0.50 g, 4.10 mmol) and 0.05 mole equiv of NaBr in a round-bottomed flask was added a stoichiometric cobalt(III) acetate (2 mole equiv) in acetic acid (30 ml). The flask was flushed with dry argon, and 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 ($MgSO_4$). Removing the ether on a rotary evaporator gave a pale-yellow oil, which was chromatographed on silica gel (hexane-ethyl acetate).

All products so formed were known compounds and their identities were confirmed by comparisons of their NMR and IR spectra with those of authentic samples.

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