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A Selective Conversion of Benzylic Alcohols to the Corresponding Carbonyl Compounds by Means of an Ag(III) Complex

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Summary. Carbonyl compounds of the type *X*PhCO*R* (R = H, Me, Ph; X = H, Me, Cl, Br) are prepared in high yields by reaction of the corresponding benzylic alcohols *X*PhCHOH*R* with $KNa_4[Ag(HIO_6)_2]\times 12H_2O$ in alkaline solution. This method allows the selective oxidation of benzylic alcohols in compounds containing other types of alcoholic functional groups.

Keywords. Alcohols; Aldehydes; Diperiodato-argentate(III) complex; Ketones; Oxidations.

Introduction

The oxidation of alcohols to aldehydes and ketones is a ubiquitous transformation in organic chemistry, and numerous oxidizing agents are available to effect this key reaction [1]. The topic raises continuous interest [2–9], but most of the reported procedures have not been applied to sensitive natural polyfunctional products. Catalysts for the preparation of different types of carbonyl compounds or carboxylic acids from alcohols have been described, but no information is available on the selective oxidation of one specific hydroxyl group in polyhydroxyl compounds.

In recent years investigators have been increasingly interested in studies of unusual oxidation states of transition metals such as Cu(III) [10–13], Ni(III) [14], Ni(IV) [15], and Ag(III) [16–19]. However, the most attention so far has been devoted to kinetic studies, whereas no information is accessible regarding synthetic applications.

We have looked more closely at the possibility of preparing carbonyl compounds with the aid of Ag(III) complexes, partly because it is unusual for Ag species to have a charge of +3, and partly because the reaction does not show considerable sensitivity to *pH*, solvent, and temperature influence. Thus, we established for the first time that the choice of the reagent can influence the regiochemical result of the reaction.

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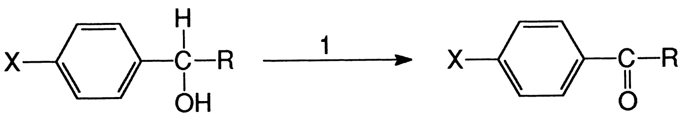
Results and Discussion

Investigations have been carried out with a series of potentially oxidable substrates to discover whether oxidation by means of potassiumtetrasodium-diperiodatoargentate(III) ($KNa_4[Ag(HIO_6)_2] \times 12H_2O$) (**1**) could be achieved. It was found that the most common open-chain alcohols (from propanol to hexadecanol) did not react. In order to initiate the reaction, the reaction conditions were varied. Higher temperature, longer reaction time, lower *pH*, different concentration of the reactants, and different solvents did not significantly affect the reaction. We also tried this oxidation reactions with some cycloalkanols, alkenols, and phenols under different reaction conditions, but only unreacted substrates remained in the reaction mixtures. Unsaturated compounds, aldehydes, and ketones were also found to be inert towards **1**.

To show the generality of this method for the oxidation of the benzylic hydroxyl group, a series of benzylic alcohols was investigated (Scheme 1).

The reactions were performed in alkaline medium in aqueous solution at room temperature or at the boiling point of the solvent depending on the substrate used. The ratio of substrate: reagent was 1:1. After usual work up the reaction products were isolated and identified. Satisfactory spectroscopic data were obtained for all products. which were characterized by GLC and by direct comparison with authentic samples. As shown in Table 1, the reaction of the benzylic alcohols **2**, **4**, **6**, **8**, **10**, and **12** leads to the formation of the corresponding carbonyl compounds **3**, **5**, **7**, **9**, **11**, and **13** in good to excellent yields.



	X	*R*	
2	H	H	**3**
4	H	CH_3	**5**
6	CH_3	CH_3	**7**
8	Cl	CH_3	**9**
10	Br	CH_3	**11**
12	Ph	Ph	**13**

Scheme 1

Table 1. Oxidation of benzylic alcohols by means of **1**

Substrate	Product	T/°C[a]	Yield/%[b]	Reaction time/min
2	**3**	r.t.	98	Immediately
4	**5**	b.p.	86	20
6	**7**	b.p.	78	45
8	**9**	b.p.	51	60
10	**11**	b.p.	63	60
12	**13**	b.p.	100	Immediately

[a] r.t: room temperature, b.p: boiling point; [b] all yields are for pure isolated products

Benzyl alcohol (**2**) and diphenyl carbinol (**12**) reacted very fast at room temperature and lead to completion in a few seconds, whereas other substrates required somewhat longer reaction times. The substituents at the aromatic ring and at the carbinol carbon atom influence the yield and the reaction rates. Weakly deactivating halogens decreased the yield of benzylic carbonyl compound compared to unsubstituted substrates; the weakly activating methyl group had less influence. Very likely the formation of the carbonyl compounds from the alcohols involves a two-electron transfer from the substrate to **1** as proposed previously from kinetic studies [16, 18].

Other recently reported oxidizing reagents are highly efficient for the oxidation of various classes of hydroxy compounds [20–23], and some of them gave cleavage products [24]. The method described in this work proceeds selectively and yields carbonyl compounds in good yields. Thus, the results indicate that **1** is the reagent of choice for the oxidation of benzylic alcohols.

In comparison with other recently reported oxidations of easily oxidable benzylic alcohols [20–23] the presented method has some additional advantages. The reaction is carried out easily and fast under mild reaction conditions without the need of complicated apparatures. On the other hand, the use of **1** allows for the selective oxidation of benzylic hydroxyl groups in polyhydroxyl compounds. Such systems occur in nature and medicine, and thus there is considerable interest in devising synthetic methods for their regioselective oxidation.

Future studies are under way to gain an insight into the mechanism of these reactions and to apply the new procedure to the oxidation of benzyl hydroxyl group containing compounds in natural products and in drug synthesis.

Experimental

Chemicals and solutions

Potassiumtetrasodium-diperiodatoargentate(III) dodecylhydrate ($KNa_4[Ag(HIO_6)_2]\times 12H_2O$, **1**) was prepared according to *Balikungeri et al.* [10]. $NaIO_4$ (Carlo Erba, 99.8–100%), KOH (Merck, *p.a.*), $AgNO_3$ (Fluka, *puriss. p.a.* ACS), $K_2S_2O_8$ (Fluka, *p.a.*), and $NaNO_3$ (Merck, *p.a.*) were used as received. All benzylic alcohols used as substrates are known compounds; some of them are commercially available, whereas **6**, **8**, **10**, and **12** were synthesized according to procedures described in the literature [25].

Typical experimental procedure

To an alkaline solution of 9.03 g **1** (10 mmol) in 100 cm^3 H_2O, 10 mmol benzylic alcohol dissolved in 10 cm^3 H_2O were added. The reaction mixture was stirred at room temperature or at the boiling point depending on the substrate used until completion of the reaction which can be judged from the change of the color of the reaction mixture. After extraction with diethyl ether ($3\times 25\,cm^3$), the organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated. The residue was distilled or crystallized to give the corresponding aldehyde or ketone.

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