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Selective Oxidation of Alcohols Using Benzyldimethyltelluronium Dichromate

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Abstract: Selective oxidation of benzylic, allylic, and saturated secondary alcohols to the corresponding aldehydes or ketones by benzyldimethyltelluronium dichromate is described.

Keywords: Alcohols, benzyldimethyltelluronium dichromate, selective oxidation

The oxidation of alcohols to the corresponding carbonyl compounds is one of the most important of all chemical transformations.^[1,2] The representative chromium-based reagents play a vital role in organic chemistry as oxidants for alcohols. For instance, pyridinium chlorochromate (PCC, Corey's reagent),^[3] pyridinium dichromate (PDC),^[4] Jones' reagent,^[5] Collins' reagent,^[6] pyridinium fluorochromate (PFC),^[7] and bipyridinium chlorochromate (BPCC)^[8] have been developed for this purpose. Some of these reagents are mild and effective oxidizing agents for alcohols, but other reagents are associated with several drawbacks such as overoxidation, poor selectivity, and use of acidic media.

Herein we report an efficient method for the selective oxidation of benzylic, allylic, and saturated secondary alcohols using benzyldimethyltelluronium dichromate. To the best of our knowledge, no attempts to use benzyldimethyltelluronium dichromate as an oxidant for oxidation of alcohols were successful.

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Benzyldimethyltelluronium dichromate was readily and safely prepared by adding an aqueous solution of potassium dichromate to an aqueous solution of benzyldimethyltelluronium bromide at room temperature. The resulting orange-yellow solid is slightly soluble in acetonitrile or dimethylformamide, air stable, and effective after long storage times.

The reactions and results are shown in Scheme 1 and Table 1, respectively. At first, we investigated the reactivity of the oxidizing agent prepared with benzylic alcohols. The oxidation of benzyl alcohol (1a) with 2 equiv. of benzyldimethyltelluronium dichromate in boiling acetonitrile gave benzaldehyde (2a) in 1 h in 95% yield. At room temperature, oxidation of benzylic alcohols with the oxidizing agent in acetonitrile or dimethylformamide was very sluggish. For example, in acetonitrile at room temperature, benzhydrol was oxidized to benzophenone in 45% yield for 24 h. During investigation, it was found that boiling acetonitrile is a suitable solvent for oxidation reaction because of its lower boiling point, higher polarity, and increased solubility of the oxidizing agent. The other solvent such as dichloromethane or

(1)	R ₁	R_2	Time (h)	(2), Yield $(\%)^a$
a	C ₆ H ₅	Н	1	95
b	m-Cl-C ₆ H ₅	Н	2	93
e	C ₆ H ₅	C_6H_5	2	93 ^b
d	C ₆ H ₅	CH_3	1	90
e	p-CH ₃ O-C ₆ H ₅	Н	1	92
ľ	C ₆ H ₅ CH=CH	Н	10	80
5	(CH ₃) ₂ C=CH(CH ₂) ₂ - CCH ₃ =CH	Н	10	82
h	(CH ₂) ₅		10	68
l	CH ₃ (CH ₂) ₃ CH ₂	CH_3	10	75
i	CH ₃ (CH ₂) ₉ CH ₂	Н	20	5
K	Cyclohexyl	Н	20	15

Table 1. Oxidation of alcohols (1) with benzyldimethyl-telluronium dichromate

^aGC yields based on alcohols (1).

^bIsolated yield.

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benzene, where the oxidizing agent was suspended, could be used but the yields and the rates were very low. This shows that the oxidation ability of the oxidizing agent apparently depends on its solubility in solvent.

Other benzylic alcohols were also transformed into the corresponding aldehydes or ketones in good to high yields. Further oxidation of aldehydes to their carboxylic acids was not observed. The oxidation of allylic alcohols (**1f**, **1g**) afforded the corresponding aldehydes with reaction times longer than that of benzylic alcohols. However, one limitation of this reaction was to give product mixtures, which appear to have been caused by (E)/(Z) isomerization during oxidation.

Interestingly, the oxidation of primary and secondary aliphatic alcohols under the same conditions revealed selectivity. Cyclohexanol (1h) and 2-heptanol (1i) as secondary alcohols were oxidized to cyclohexanone and 2-heptanone, respectively, in 68% and 75% yields in 10h, whereas 1-dodecanol (1j) and cyclohexylmethanol (1k) as primary alcohols gave the corresponding aldehydes, respectively, only 5% and 15% in 20h. This showed a possibility of selective oxidation potential, different from other oxidizing agents. The chemoselective oxidation of a specific alcohol in the presence of other oxidizable hydroxyl groups is particularly useful in organic synthesis. Therefore, the chemoselectivity of this oxidizing agent to the oxidation of diol compounds was further examined. As shown in Scheme 2, 1-phenyl-1,3-propandiol (3) having a benzylic and a saturated primary hydroxyl group under the same reaction conditions was oxidized to 3-hydroxy-1-phenyl-1-propanone $(4)^{[9]}$ in 4 h in 75% yield without affecting a saturated primary hydroxyl group. Similarly, compound (5) was also transformed into the corresponding hydroxyl ketone $(6)^{[\bar{0}]}$ in 5 h in 67% yield.

It is noteworthy that good selectivity was observed in the selective oxidation of benzylic and allylic alcohols that have saturated aliphatic alcohols.



Scheme 2.

In conclusion, benzyldimethyltelluronium dichromate as an oxidizing agent was effective for the selective oxidation of benzylic, allylic, and saturated secondary alcohols.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. ¹H NMR spectra recorded in CDCl₃ on a Varian VXR-300 instrument at 300 MHz with TMS as internal standard. IR spectrum was measured in KBr on an FT Alpha Centauri FT-IR spectrophotometer.

Preparation of Benzyldimethyltelluronium Dichromate

Dimethyltelluronium^[10] (3.14 g, 20 mmol) was added slowly to a solution of benzyl bromide (3.42 g, 20 mmol) in methanol (20 mL) and the mixture was stirred at room temperature for 2 h. On standing, benzyldimethyltelluronium bromide (white solid) was formed, filtered off, and dried. Yield: 6.10 g (92%); mp 149–150°C. A solution of potassium dichromate (1.47 g, 5 mmol) in water (50 mL) was added slowly to a solution of benzyldimethyl-telluronium bromide (3.27 g, 10 mmol) in water (180 mL) at room temperature. After stirring the resulting solution for 1 h, the precipitate was collected by filtration and dried in vacuo for 3 h to give the orange-yellow solid. Yield: 3.14 g (88%); mp 142–143°C. IR (KBr): 935, 880, 770, 730 cm⁻¹ (dichromate ion).^[11] Anal. found: C, 30.10; H, 3.88. Calcd. for $C_{18}H_{26}O_7Cr_2Te_2$: C, 30.29; H, 3.67.

Oxidation of Alcohols (1) to Carbonyl Compounds (2): General Procedure

Benzyldimethyltelluronium dichromate (2 mmol) was added to a stirred solution of an alcohol (1 mmol) in acetonitrile (25 mL). The reaction mixture was stirred for 1-20 h under reflux. After completion of the reaction, the mixture was filtered and extracted with ether. The extract was dried and evaporated to dryness, and a portion was analyzed by GC with the authentic samples.

Selective Oxidation of 1,3-Diols (3), (5) to Carbonyl Compounds (4), (6)

Benzyldimethyltelluronium dichromate (2 mmol) was added to a stirred solution of (3) or (5) (1 mmol) in acetonitrile (25 mL). The reaction mixture

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was stirred for 4-5 h under reflux. After completion of the reaction, workup as described previously followed by flash column chromatography on silica gel (ethyl acetate/hexane, 1:1) gave the product (**4**) in 75% yield or the product (**6**) in 67% yield, respectively. Spectral data of the products were identical with those reported.^[9]

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