

Barium dichromate [BaCr₂O₇], a mild reagent for oxidation of alcohols to their corresponding carbonyls in non-aqueous polar aprotic media

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Abstract—Barium dichromate is used as a mild oxidizing agent for the selective conversion of primary and secondary alcohols to their corresponding aldehydes and ketones, respectively. Over-oxidation does not occur and primary alcohols undergo oxidation to the aldehyde. Primary and secondary benzylic alcohols are oxidized faster and more efficiently.
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Chromium-based oxidations are the most widely used of all oxidation reactions. These methods have been developed and modified to improve selectivities. However, these methods are associated with several drawbacks.

Over-oxidation, removal of the products from toxic chromium contaminants, non-selectivity, use of strongly acidic media and other problems are encountered with these methods.

For instance, sodium dichromate in aqueous sulfuric acid is limited by over-oxidation.¹ Two-phase oxidations have been developed for the oxidation of acid-sensitive reactants and products.² Phase transfer conditions have been used for substances with limited solubility in aqueous media.³ Cr(VI)/aq H₂SO₄/acetone converts saturated primary alcohols to the corresponding acids.⁴ Other well-known chromium-based oxidants such as pyridinium chlorochromate (PCC),⁵ pyridinium fluorochromate (PFC),⁶ bipyridinium chlorochromate (BPCC)⁷ and pyridinium dichromate (PDC),⁸ also have advantages and disadvantages.

In this work we utilized barium dichromate as an oxidant in acetonitrile, a polar non-aqueous aprotic solvent. Recently the use of barium permanganate was

reported as a mild and efficient oxidizing agent for selective deoxygenation of benzylic oximes to their corresponding carbonyl compounds and also for oxidation of different types of primary and secondary hydroxy compounds in the same solvent.^{9–11}

Oxidation reactions were attempted with aliphatic and benzylic alcohols in boiling acetonitrile. During our investigations we found that barium permanganate is slightly soluble in polar aprotic solvents especially in acetonitrile, and this results in a mild oxidation potential, different from other manganese oxyanions.

We now report that barium dichromate¹² is a suitable oxidizing agent for the conversion of alcohols to their corresponding carbonyl compounds in boiling acetonitrile or dioxane. Acetonitrile is a suitable solvent because of its lower boiling point and higher polarity than dioxane. Non-polar solvents are not suitable for these conversions because of the insolubility of barium dichromate in such solvents.

Primary alcohols undergo oxidation to produce aldehydes in moderate to good yields (63–85%) (Table 1).

Secondary alcohols gave ketones in good to excellent yields (72–98%) (Table 2).

Products were purified by chromatographic methods and the structures verified with spectroscopic methods and by comparing their physical properties with those of known compounds.

Keywords: Barium dichromate; Oxidation; Oxidizing agent; Non-aqueous media.

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Table 1.

$$\text{RCH}_2\text{OH} \xrightarrow[\text{reflux, 2.5-4 h, Oxidant / Reactant: 2/1}]{\text{BaCr}_2\text{O}_7, \text{MeCN}} \text{RCHO}$$

63-85%

Entry	R	Yield (%)
A	Me-	63
B	Et-	65
C	Ph-	85
D	PhCH ₂ -	63
E	PhCH=CH-	75

Table 2.

$$\text{R}^1\text{R}^2\text{CH-OH} \xrightarrow[\text{reflux, 0.75-4 h, Oxidant / Reactant: 2/1}]{\text{BaCr}_2\text{O}_7, \text{MeCN}} \text{R}^1\text{R}^2\text{C=O}$$

72-98%

Entry	R ¹ , R ²	Yield (%)
F	Me, Me	85
G	Me, Et	87
H	-(CH ₂) ₅ -	72
I	Me, Ph	92
J	Ph, Ph	98
K	Ph, <i>p</i> -C ₆ H ₄ -OH	96
L	Ph, PhCH ₂	90

Barium dichromate: BaCr₂O₇ was obtained by dissolving barium chromate in concentrated chromic acid (75% solution of CrO₃ in distilled water) at 85–90 °C. On cooling, red crystals of the compound BaCr₂O₇ · 2H₂O were deposited, which lose water at 100 °C. The dried material was stored in a capped bottle.

Oxidation of cyclohexanol to cyclohexanone as a typical procedure: A mixture of barium dichromate (354 mg, 3 mmol) and cyclohexanol (150 mg, 1.5 mmol) in acetonitrile (12 mL) was stirred for 4 h under reflux. The progress of reaction was followed by gas chromatography. The reaction mixture was filtered, the solvent was

removed and the residue was purified using petroleum ether (bp 60–80 °C) as eluent on a silica gel column. Evaporation of the solvent gave pure cyclohexanone (106 mg, 72%).

Oxidation of benzhydrol to benzophenone as a typical procedure: A mixture of barium dichromate (354 mg, 3 mmol) and benzhydrol (184 mg, 1 mmol) in acetonitrile (10 mL) was stirred for 0.75 h under reflux. The progress of reaction was followed by TLC. The reaction mixture was filtered, the solvent was removed and the residue was purified using *n*-hexane/Et₂O (80:20) as eluent on a silica gel column. Evaporation of the solvent gave pure benzophenone (178 mg, 98%).

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