Barium Dichromate, An Oxidizing Agent For Conversion Of Thiols To Their Corresponding Disulfides Under Nonaqueous Polar Aprotic Media

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ABSTRACT
Barium dichromate is used as an efficient oxidizing agent for the conversion of different types of thiols to their corresponding disulfides. Overoxidation does not occur and both aromatic and aliphatic thiols undergo oxidation in the same manner.

INTRODUCTION
This method has been developed and modified to improve selectivities. The use of strongly acidic media and other problems are encountered with these methods.

For instance, sodium dichromate in aqueous sulphuric acid is limited by overoxidation[1]. Cr(VI)/aq. H₂SO₄/acetone converts saturated primary alcohols to the corresponding acids[2]. Other well known chromium based oxidants such as pyridinium chlorochromate [PCC][3], pyridinium fluorochromate [PFC][4], bipyridinium chlorochromate [BPCC][5], pyridinium dichromate [PDC][6], have also advantages and disadvantages.

In this work we utilized barium dichromate as an oxidant in acetonitrile. Recently the use of barium dichromate was reported as a mild and efficient oxidizing agent in the same solvent for the conversion of different types of alcohols to their corresponding carbonyl compounds[7]. Also the use of barium permanganate have been reported as a mild and efficient oxidizing agent in the same solvent[8-10].

In our investigation, oxidation reactions were attempted with aliphatic and benzylc thiols in boiling acetonitrile. Barium dichromate is slightly soluble...
in polar aprotic solvents especially in acetonitrile. This results in a mild oxidation potential, different from other chromate oxyanions.

In this work we denote barium dichromate is a suitable oxidizing agent for coupling of thiols to their corresponding disulfide compounds in boiling acetonitrile. The acetonitrile is a suitable solvent because of its low boiling point and high polarity. Nonpolar solvents are not suitable for these conversions because of insolvency of barium dichromate.

Aliphatic and aromatic thiols undergo oxidation to produce disulfides in quantitative yields (90-98\%) (TABLE 1).

\[
\text{2 RSH} \xrightarrow{\text{BaCr}_2\text{O}_7, \text{MeCN}} \text{RSSR} \quad \text{reflux, 2.5-4 h, 90-98\%}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Oxidant / Reactant</th>
<th>Yield % (isolated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>n-Pr-</td>
<td>2/1</td>
<td>93</td>
</tr>
<tr>
<td>b</td>
<td>n-Bu-</td>
<td>2/1</td>
<td>95</td>
</tr>
<tr>
<td>c</td>
<td>n-Octyl-</td>
<td>2/1</td>
<td>98</td>
</tr>
<tr>
<td>d</td>
<td>Cyclohexyl-</td>
<td>2/1</td>
<td>90</td>
</tr>
<tr>
<td>e</td>
<td>Ph-</td>
<td>2/1</td>
<td>95</td>
</tr>
<tr>
<td>f</td>
<td>PhCH2-</td>
<td>2/1</td>
<td>94</td>
</tr>
<tr>
<td>g</td>
<td>p-BrC6H4-</td>
<td>2/1</td>
<td>98</td>
</tr>
<tr>
<td>h</td>
<td>p-MeC6H4-</td>
<td>2/1</td>
<td>98</td>
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<tr>
<td>i</td>
<td>o-C6C6H4-</td>
<td>2/1</td>
<td>96</td>
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<tr>
<td>j</td>
<td>2-Naphthyl-</td>
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<td>95</td>
</tr>
<tr>
<td>k</td>
<td>2-Benzothiazole-</td>
<td>2/1</td>
<td>94</td>
</tr>
</tbody>
</table>

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

**EXPERIMENTAL**

Barium dichromate was obtained by dissolving barium chromate in hot concentrated chromic acid. On cooling, red crystals of the composition BaCrO₄·2H₂O was deposited, which lose water at 100°C. The dried crystals was stored in a capped bottle.

**Oxidation of cyclohexyl mercaptane to cyclohexane disulfide**

A mixture of barium dichromate (354 mg, 3 mmol) and cyclohexyl mercaptane (174 mg, 1.5 mmol) in acetonitrile (15 ml) was stirred for 4h under reflux.

The progress of reaction was followed with gas chromatography. The reaction mixture was filtered, the solvent was removed by evaporation and pure cyclohexyl disulfide [155 mg, 90\%] was obtained.

**Oxidation of p-bromo-thiophenol to 4,4′-benzenedisulfide**

A mixture of barium dichromate (354 mg, 3 mmol) and p-bromo-thiophenol (283 mg, 1.5 mmol) in acetonitrile (15 ml) was stirred for 3 h under reflux. The progress of reaction was followed by TLC. The reaction mixture was filtered, the solvent was removed by evaporation of the solvent. Pure 4,4′-benzene disulfide was obtained [184 mg, 98\%].

**ACKNOWLEDGEMENT**

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**REFERENCES**