Trichloroisocyanuric Acid (TCCA)

Compiled by José C. Barros

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Introduction

Trichloroisocyanuric acid (TCCA) is a stable and inexpensive industrial chemical usually used as bleaching agent and bactericide.

It has found applications in organic chemistry as a chlorinating agent or oxidant, allowing thioacetalization of carbonyl compounds, conversion of alcohols to halides, carboxylic acids to acid chlorides, alkenes to chloroethers, N-nitrosation of N,N-dialkylamines, selective mononitration of phenols, oxidation of alcohols to carbonyl compounds, aldehydes to methyl esters, aldoximes to nitrile oxides, thiols to disulfides, selenols to diselenides, and sulfides to sulfoxides.

Preparation

TCCA (1) is prepared by chlorination of cyanuric acid (2) with chlorine gas (Scheme 1). It is readily soluble in organic solvents.

Abstracts

(A) Amides, lactams and carbamates of α-amino acids can be easy transformed into the corresponding N-chlorinated compounds through reaction with TCCA, under mild reaction conditions.

(B) Primary alcohols are oxidized to acids using stoichiometric TCCA and catalytic RuCl₃ in the presence of n-Bu₄NBr and K₂CO₃ in MeCN/H₂O. Secondary alcohols are oxidized to ketones in the same set using MeCN/H₂O or EtOAc/H₂O. Effects of pH, solvent and base were also studied.

(C) Oxidation of 1,3,5-trisubstituted pyrazolines to the corresponding pyrazoles is achieved using TCCA under both heterogeneous and solvent-free conditions.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>octanol</td>
<td>octanoic acid</td>
<td>95</td>
</tr>
<tr>
<td>2-octanol</td>
<td>2-octanone</td>
<td>98</td>
</tr>
<tr>
<td>cyclopentanol</td>
<td>cyclopentanone</td>
<td>90</td>
</tr>
</tbody>
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(D) Combination of TCCA and catalytic TEMPO in CH₂Cl₂ leads to the conversion of primary alcohols into aldehydes. In the presence of acetone, NaBr and NaHCO₃, acids are obtained. Secondary alcohols are oxidized to ketones.

(E) Dinitrophenols are obtained upon reaction of phenols with TCCA, NaN₂O and wet SiO₂ under solid-phase reaction via in situ generation of HNO₂.

(F) Epoxides can be produced in mild conditions by reaction of alkenes with trichloroisocyanuric acid in aqueous acetone followed by treatment of resulting chlorohydrin with aqueous KOH in Et₂O/pentane.

(G) Primary amines are successfully converted into nitriles by means of TCCA and catalytic TEMPO under mild conditions. Other functional groups remain unaffected.

(H) Amino acids are cleanly and efficiently converted into nitriles by means of a decarboxylation reaction carried out with TCCA in water or methanol in the presence of pyridine. Using TCCA, (S)-(+)-2-methylbutyronitrile is obtained at the highest optical purity.

(I) Aldoximes derived from an o-protected vanillin, when treated with TCCA in the presence of olefins as dipolarophiles, afford nitrile oxides. Subsequent 1,3-dipolar cycloaddition generates the corresponding isoxazolines.

References