

SYNLETT Spotlight 132

Trichloroisocyanuric Acid (TCCA)

Compiled by José C. Barros



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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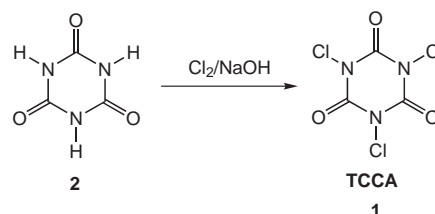
Introduction

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,¹ 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

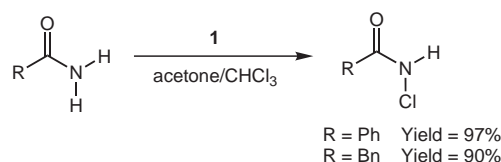
TCCA (**1**) is prepared by chlorination of cyanuric acid (**2**) with chlorine gas (Scheme 1).² It is readily soluble in organic solvents.



Scheme 1

Abstracts

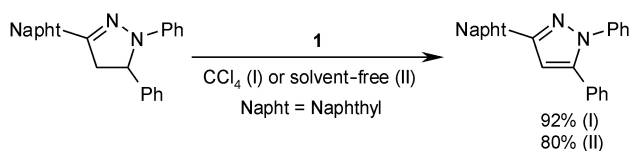
(A) Amides, lactams and carbamates of α -amino acids can be easily transformed into the corresponding N-chlorinated compounds through reaction with TCCA, under mild reaction conditions.³



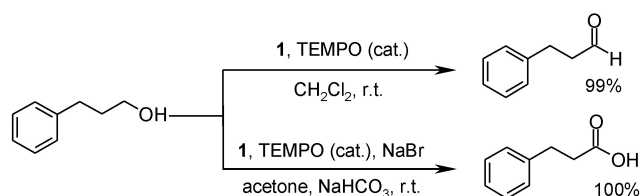
(B) Primary alcohols are oxidized to acids using stoichiometric TCCA and catalytic RuCl_3 in the presence of *n*- Bu_4NBr and K_2CO_3 in $\text{MeCN}/\text{H}_2\text{O}$. Secondary alcohols are oxidized to ketones in the same set using $\text{MeCN}/\text{H}_2\text{O}$ or $\text{EtOAc}/\text{H}_2\text{O}$. Effects of pH, solvent and base were also studied.⁴

Substrate	Product	Yield (%)
octanol	octanoic acid	95
2-octanol	2-octanone	98
cyclopentanol	cyclopentanone	90

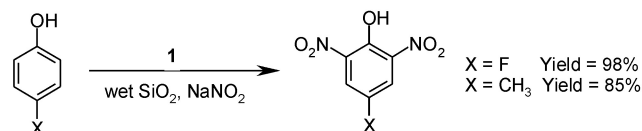
(C) Oxidation of 1,3,5-trisubstituted pyrazolines to the corresponding pyrazoles is achieved using TCCA under both heterogeneous and solvent-free conditions.⁵



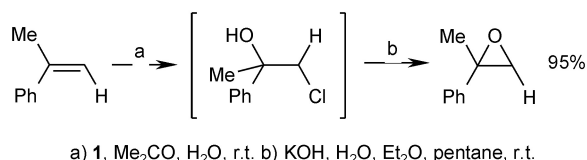
(D) Combination of TCCA and catalytic TEMPO in CH_2Cl_2 leads to the conversion of primary alcohols into aldehydes.⁶ In the presence of acetone, NaBr and NaHCO_3 , acids are obtained.⁷ Secondary alcohols are oxidized to ketones.



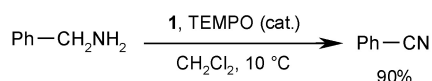
(E) Dinitrophenols are obtained upon reaction of phenols with TCCA, NaNO_2 and wet SiO_2 under solid-phase reaction via in situ generation of HNO_2 .⁸



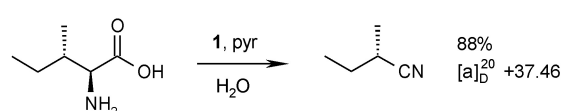
(F) Epoxides can be produced in mild conditions by reaction of alkenes with trichloroisocyanuric acid in aqueous acetone followed by treatment of resulting chlorohydrin with aqueous KOH in Et_2O /pentane.⁹



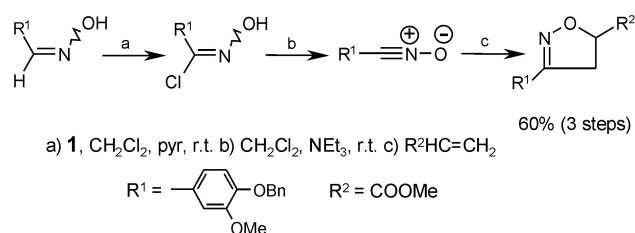
(G) Primary amines are successfully converted into nitriles by means of TCCA and catalytic TEMPO under mild conditions. Other functional groups remain unaffected.¹⁰



(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.¹¹



(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.¹²



References

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