

BCl₃-2-Chloroethanol, 10% w/w

Product Specification

At one time diazomethane and other diazoalkanes were popular reagents for esterification, but their use has diminished because of the explosion hazards and carcinogenicity of these materials. Boron trichloride and boron trifluoride are now the popular esterification reagents. Under very mild conditions, reagents consisting of boron trihalide in 2-chloroethanol, methanol, or butanol readily form esters of aliphatic and aromatic acids, including certain hindered structures, without altering relatively labile structures. The reaction is nearly instantaneous in many cases, and requires only a few minutes reflux in other cases.*

BCl₃-2-Chloroethanol, 10% w/w (10% boron trichloride in 2-chloroethanol) is particularly useful for preparing esters of phenoxy-type acids (e.g., acid herbicides), and for preparing analytes for electron capture detection (ECD). When the reagent and sample are heated in a sealed vessel for a short time, the analytes are combined with the anhydrous alcohol (2-chloroethanol) in the presence of the acid catalyst (BCl₃). In the reaction, the analyte and alcohol molecules are joined with a loss of water. The derivatives can be quickly and easily recovered, quantitatively, from the esterification medium and analyzed by GC.

Derivatization with 2-chloroethanol facilitates electron capture detection. An ECD responds well to very low concentrations of molecules containing electron-capturing halogen atoms and, to a lesser extent, nitro and carbonyl groups. Sensitivity of detection with an ECD improves as the number of these groups in the molecule is increased. However, multiple electron-capturing groups also can increase the retention time of an analyte.

Applications/Benefits

Used for esterifying/halogenating compounds for electron capture detection.

Used for preparing phenoxy acids (acid herbicides).

Used to decrease sample volatility.

Typical Procedure

This procedure is intended to be a guideline and may be adapted as necessary to meet the needs of a specific application. Always take proper safety precautions when using an esterification reagent – consult MSDS for specific handling information.

Prepare a reagent blank (all components, solvents, etc., *except sample*), following the same procedure as used for the sample.

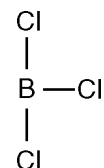
1. Weigh 1-5mg of sample (acid) into a 5mL reaction vessel. If appropriate, dissolve sample in nonpolar organic solvent (e.g., hexane, ether, toluene). If sample is in aqueous solution, evaporate to dryness, then use neat or add organic solvent.
2. Add 1 mL BCl₃-2-chloroethanol, 10% w/w. A water scavenger (e.g., 2,2-dimethoxypropane) can be added at this point. (Water can prevent the reaction from going to completion, producing low yields.)
3. Heat at 90°C for 5-10 minutes. Cool, then add 1 mL water and 1 mL hexane or other nonpolar solvent.
4. Shake the reaction vessel – it is critical to get the esters into the nonpolar solvent.
5. Carefully remove the upper (organic) layer, and dry it over anhydrous sodium sulfate.

It may be necessary to dilute the sample to an appropriate concentration for GC-ECD analysis: 0.05-1pg for organohalogen or 50ppt-1ppm for chlorinated solvents and pesticides.

Properties

Boron Trichloride

Structure:



CAS Number: 10294-34-5

Molecular Formula: BCl₃

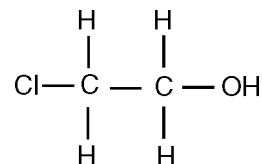
Formula Weight: 117.19

bp: 12.5°C

Appearance: colorless gas

2-Chloroethanol

Structure:



CAS Number: 107-07-3

Molecular Formula: ClCH₂CH₂OH

Formula Weight: 80.51

bp: 129°C

Flash Point: 140°F (60°C)

d: 1.201

n_D: 1.4410 at 20°C

Appearance: clear colorless liquid

796-0600, 0601

6. To determine when derivatization is complete, analyze aliquots of the sample at selected time intervals until no further increase in product peak(s) is observed.

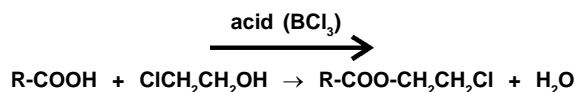
Derivatization times vary widely, depending upon the specific compound(s) being derivatized. If derivatization is not complete, use additional reagent (excess of 2-chloroethanol is needed, relative to the acid or ester) or reevaluate temperature/time.

* Esterification is best in the presence of a volatile catalyst, which subsequently can be removed along with excess alcohol. In addition to boron trichloride and boron trifluoride, typical catalysts are hydrogen chloride (favored because of its acid strength and ready removal at the end of the reaction), sulfuric acid (less easily removed and has dehydrating reactions, charring effects, and/or oxidative side reactions), trifluoroacetic and dichloroacetic acids, benzene- and p-toluene-sulfonic acids, sulfuric and thionyl chlorides, phosphorus trichloride and oxychloride, and polyphosphoric acids. The catalyst must be chosen with care to avoid isomerization and artifact production with unsaturated or cyclopropane-substituted acids. One of the main advantages of BCl₃ over certain fluorine-containing catalysts is that it does not produce fluoroanhydrides on acylation with acid anhydrides and does not form HF when phenols or alkyl ethers of phenols are acylated by acids.

Alternatively, analytes can be esterified with more reactive acid anhydrides or chlorides, for which no catalyst is required.

Mechanism (1,2,3)

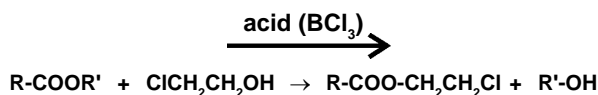
Esterification



Adapted from (1).

Esterification involves heating the carboxylic acid with an acid catalyst in an alcohol solvent. The catalyst protonates an oxygen atom of the COOH group, making the acid much more reactive to nucleophiles. An alcohol molecule (ClCH₂CH₂OH) then combines with the protonated acid, to yield the ester product (R-COO-CH₂CH₂Cl) with loss of water. Esterification is a reversible reaction. Water must be removed to drive the reaction to the right and obtain a high ester yield. A chemical reagent can be used to remove water as it is formed or, if the reaction is conducted at a temperature above 100°C, water may distill off as it is formed. 2,2-dimethoxypropane can be introduced into the reaction mixture to react with the water, yielding acetone. Other water scavengers are anhydrous sulfuric acid and graphite bisulfate.

Transesterification



Adapted from (3).

In transesterification, the alcohol is displaced from the ester by another alcohol (e.g., 2-chloroethanol) in a process similar to hydrolysis (the second alcohol is used instead of water), forming a new ester. Transesterification also is an equilibrium reaction. To shift the reaction to the right, it is necessary to use a large excess of the second alcohol, or to remove one of the products from the reaction mixture. The stoichiometry of the reaction requires 3 moles of alcohol for each mole of triglyceride. Conversion is maximized if excess alcohol is used. The conversion rate also is influenced by the reaction temperature – the reaction generally is conducted near the boiling point of the alcohol.

Toxicity - Hazards - Storage - Stability

BCl₃-2-chloroethanol may irritate eyes, skin, and/or the respiratory system. Recommended storage conditions for the unopened product are stated on the label. Store opened reagent in a sealed bottle or ampul. **If you store an opened container or transfer the contents to another container for later reuse validate that your storage conditions adequately protected the reagent.**

Use only in a well ventilated area and keep away from ignition sources. Moisture can hinder the reaction – it may be necessary to dry the solvents before conducting the reaction.

The reagent has a limited shelf-life, even when refrigerated, and the use of old or excessively concentrated solutions (through alcohol evaporation) often produces artifacts and a significantly lower reaction yield.

Ordering Information:

BCl₃-2-Chloroethanol, 10% w/w

10 x 1mL	33056-U
10mL	33055-U

Microreaction Vessels with Hole Caps and Septa

pk. of 12	
1 mL	33293
3 mL	33297
5 mL	33299

Books

<i>Handbook of Derivatives for Chromatography</i> K. Blau and J. Halket	Z246220
<i>Handbook of Analytical Derivatization Reactions</i> D.R Knapp	23561

Additional Reading

- N.P. Hill, A.E. McIntyre, R. Perry, J.N. Lester *Development of a Method for the Analysis of Chlorophenoxy-Herbicides in Waste Waters and Waste Water Sludges* Int. J. Environ. Anal. Chem., **15**: 107-130 (1983).
- I.O.O. Korhonen *Gas-Liquid Chromatographic Analyses. XLVI. Separation of C3 to C5 Branched-Chain, C3 to C6 Unsaturated and Ethyl and omega-Chloroethyl Esters of Benzoic, 4-Nitrobenzoic and 3,5 Dinitrobenzoic Acids on SE 30 and OV 351 Capillary Columns with Temperature-Programming* J. Chromatogr., **357**: 107-118 (1986).
- A. Horna, K. Komarek, J. Churacek, O. Dufka *Glass-Capillary Gas Chromatography-Mass Spectrometry of Mixtures of Isomeric Halogenated Esters of Carboxylic Acids* J. Chromatogr., **290**: 45-55 (1984).
- D. L. Heikes and K.R. Griffitt *Mass-Spectrometric Identification and Gas-Liquid Chromatographic Determination of 2-Chloroethyl Esters of Fatty Acids in Spices and Foods* JAOAC, **62**: 768-791 (1979).

References

1. K. Blau and J. Halket *Handbook of Derivatives for Chromatography* (2nd ed.) John Wiley & Sons, New York, 1993.
 2. D.R. Knapp *Handbook of Analytical Derivatization Reactions* John Wiley & Sons, New York, 1979.
 3. *Bailey's Industrial Oil and Fat Products*, fifth edition, Vol. 5, John Wiley & Sons, New York (1995).
 4. K.J. Hyver *High Resolution Gas Chromatography* Hewlett Packard, 1989.
- References not available from Supelco.

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