

# Product Information

## 91379 Boron trichloride solution

12% in methanol, for GC derivatization, LiChropur®

**Storage temperature: -20°C**

Boron trichloride and boron trifluoride are popular esterification reagents. Under very mild conditions, these reagents 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.\*

12% Boron trichloride solution in methanol is particularly useful for preparing methyl esters of carboxylic acids and esters. When the reagent and sample are heated in a sealed vessel for a short time, the analytes are joined with the anhydrous alcohol (methanol) in the presence of the Lewis acid catalyst ( $\text{BCl}_3$ ) with a loss of water. The derivatives can be quickly and easily recovered, quantitatively, from the esterification medium and analyzed by GC.

### Applications/Benefits

Used for derivatizing carboxylic acids and transesterifying esters. Particularly useful for derivatizing carboxylic acids in bacterial lipids and seed oils. Provides convenient, fast, quantitative esterification/transesterification. Clean reaction (no side reactions) with volatile by-products. More stable than  $\text{BF}_3$ -methanol at room temperature ( $\text{BCl}_3$  is not as volatile as  $\text{BF}_3$ ).

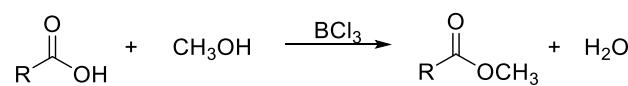
### Typical Procedure

This procedure is intended to be a guideline and may be adapted as necessary to meet the needs of a specific application. Prepare a reagent blank (all components, solvents, etc., except sample), following the same procedure as used for the sample.

1. Weigh 1-25 mg 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 2 mL Boron trichloride solution. 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 60°C for 5-10 minutes. Cool, then add 1 mL water and 1mL hexane.
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.
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 methanol is needed, relative to the acid or ester) or reevaluate temperature/time.

### Mechanism<sup>1-3</sup> Esterification

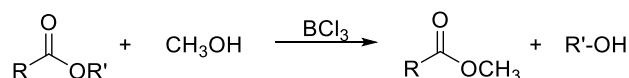


Esterification involves heating the carboxylic acid with an acid catalyst in an alcohol solvent. The catalyst protonates an oxygen atom of the  $\text{CO}_2\text{H}$  group, making the acid much more reactive to nucleophiles.



A methanol molecule then combines with the protonated acid, to yield the methyl ester product ( $\text{R}-\text{COO}-\text{CH}_3$ ) 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



In transesterification, the alcohol is displaced from the ester by another alcohol (e.g., methanol) 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. 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.

## Storage/Stability

Recommended storage conditions for the unopened product are stated on the label. Store opened reagent in a sealed bottle or ampule. 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.

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## References

1. K. Blau and J. Halket, *Handbook of Derivatives for Chromatography* (2<sup>nd</sup> 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.

## Precautions and Disclaimer

This product is for R&D use only, not for drug, household, or other uses.

Please consult the Safety Data Sheet for information regarding hazards and safe handling practices.

\* 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-toluenesulfonic acids, sulfonyl 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  $\text{BCl}_3$  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.

