

# BF<sub>3</sub>-Butanol, 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.\*

**BF<sub>3</sub>-Butanol, 10% w/w** (10% boron trifluoride in butanol) is particularly useful for preparing n-butyl esters of a variety of mono- and dicarboxylic acids, including saturated straight and branched short chain (C1-C10) fatty acids, 2-hydroxy and 2-keto fatty acids, and simple aromatic acids. Although many of the monocarboxylic acids are sufficiently volatile for GC analysis, derivatization improves peak shape and reduces adsorption losses. For dicarboxylic acids and many multifunctional carboxylic acids, derivatization is essential for successful GC analysis.

When the reagent and sample are heated in a sealed vessel for a short time, the analytes are combined with the anhydrous alcohol (n-butanol) in the presence of the acid catalyst (BF<sub>3</sub>). 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.

### Applications/Benefits

Used for preparing short chain (C1-C10) monocarboxylic and dicarboxylic acids for GC.

Provides convenient, fast, quantitative esterification of fatty acids or transesterification of esters.

Clean reaction (no side reactions) with volatile by-products.

Resulting n-butyl esters are stable, volatile, and water soluble.

### 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.

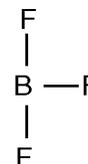
Prepare a reagent blank (all components, solvents, etc., *except sample*), following the same procedure as used for the sample.

1. Weigh 25-100mg 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 2mL BF<sub>3</sub>-butanol, 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 60°C for 5-10 minutes. Cool, then add 1mL water and 1mL hexane.
4. Neutralize, then remove excess butanol by adding a saturated solution of sodium chloride.
5. Shake the reaction vessel – it is critical to get the esters into the nonpolar solvent.
6. Carefully remove the upper (organic) layer, and dry it over anhydrous sodium sulfate.

### Properties

#### Boron Trifluoride

Structure:



CAS Number: 7637-07-2

Molecular Formula: BF<sub>3</sub>

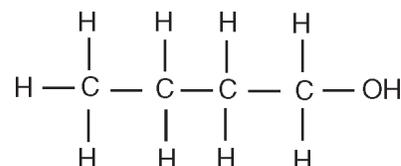
Formula Weight: 67.82

bp: -100.4°C

Appearance: colorless gas with pungent odor

#### n-Butanol

Structure:



CAS Number: 71-36-3

Molecular Formula: CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>OH

Formula Weight: 74.12

bp: 117.7°C

Flash Point: 95°F (35°C)

d: 0.810

n<sub>D</sub>: 1.3990 at 20°C

Appearance: clear colorless liquid

796-0597,0599

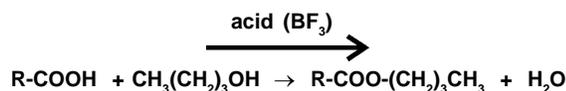
7. To determine when derivatization is complete, analyze aliquots of the sample at selected time intervals until no further increase in product peak(s) is observed.

Derivatization times vary widely, depending upon the specific compound(s) being derivatized. If derivatization is not complete, use additional reagent (excess of n-butanol 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, sulfuryl 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 BF<sub>3</sub> over other fluorinated 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)

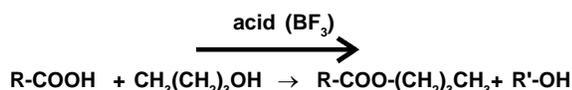
### Esterification



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 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>OH) then combines with the protonated acid, to yield the ester product (R-COO-(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) 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., n-butanol) 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

BF<sub>3</sub>-butanol is a flammable, toxic liquid. It 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:

#### BF<sub>3</sub>-Butanol, 10% w/w

10 x 5mL	33126-U
30mL	33348
100mL	33125-U

#### Microreaction Vessels with Hole Caps and Septa

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

#### Books

*Handbook of Derivatives for Chromatography*  
K. Blau and J. Halket **Z246220**

*Handbook of Analytical Derivatization Reactions*  
D.R Knapp **23561**

#### Additional Reading

F. Sakaguchi and K. Kawamura *Identification of 4-Oxoheptanedioic Acid in the Marine Atmosphere by Capillary Gas Chromatography-Mass Spectrometry J. Chromatogr.*, **687**: 315-321 (1994).

K. Kawamura *Identification of C2-C10 omega-Oxocarboxylic Acids, Pyruvic Acid and C2-C3 alpha-Dicarbonyls in Wet Precipitation and Aerosol Samples by Capillary GC and GC-MS Anal. Chem.*, **65**: 3505-3511 (1993).

J.L. Iverson and A.J. Sheppard *Determination of Fatty Acids in Butter Fat, Using Temperature-Programmed Gas Chromatography of the Butyl Esters Food Chem.*, **21**: 223-234 (1986).

J.K. Khandelwal, T. Kline, J.P. Green *Measurement of Imidazolylacetic Acid in Urine by Gas Chromatography-Mass Spectrometry J. Chromatogr., Biomed. Appl.*, **44 (2)** (J. Chromatogr., 343), 249-257 (1985).

#### 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).

References not available from Supelco.

Contact our Technical Service Department (phone 800-359-3041 or 814-359-3041, FAX 800-359-3044 or 814-359-5468) for expert answers to your questions.

For more information, or current prices, contact your nearest Supelco subsidiary listed below. To obtain further contact information, visit our website ([www.sigma-aldrich.com](http://www.sigma-aldrich.com)), see the Supelco catalog, or contact Supelco, Bellefonte, PA 16823-0048 USA.

**ARGENTINA** · Sigma-Aldrich de Argentina, S.A. · Buenos Aires 1119 **AUSTRALIA** · Sigma-Aldrich Pty. Ltd. · Castle Hill NSW 2154 **AUSTRIA** · Sigma-Aldrich Handels GmbH · A-1110 Wien  
**BELGIUM** · Sigma-Aldrich N.V./S.A. · B-2880 Bornem **BRAZIL** · Sigma-Aldrich Quimica Brasil Ltda. · 01239-010 São Paulo, SP **CANADA** · Sigma-Aldrich Canada, Ltd. · 2149 Winston Park Dr., Oakville, ON L6H 6J8  
**CZECH REPUBLIC** · Sigma-Aldrich s.r.o. · 186 00 Praha 8 **DENMARK** · Sigma-Aldrich Denmark A/S · DK-2665 Vallensbaek Strand **FINLAND** · Sigma-Aldrich Finland/YA-Kemia Oy · FIN-00700 Helsinki  
**FRANCE** · Sigma-Aldrich Chimie · 38297 Saint-Quentin-Fallavier Cedex **GERMANY** · Sigma-Aldrich Chemie GmbH · D-82041 Deisenhofen **GREECE** · Sigma-Aldrich (o.m.) Ltd. · Ilioupoli 16346, Athens  
**HUNGARY** · Sigma-Aldrich Kft. · H-1067 Budapest **INDIA** · Sigma-Aldrich Co. · Bangalore 560 048 **IRELAND** · Sigma-Aldrich Ireland Ltd. · Dublin 24 **ISRAEL** · Sigma Israel Chemicals Ltd. · Rehovot 76100  
**ITALY** · Sigma-Aldrich s.r.l. · 20151 Milano **JAPAN** · Sigma-Aldrich Japan K.K. · Chuo-ku, Tokyo 103 **KOREA** · Sigma-Aldrich Korea · Seoul **MALAYSIA** · Sigma-Aldrich (M) Sdn. Bhd. · 58200 Kuala Lumpur  
**MEXICO** · Sigma-Aldrich Quimica S.A. de C.V. · 50200 Toluca **NETHERLANDS** · Sigma-Aldrich Chemie BV · 3330 AA Zwijndrecht **NORWAY** · Sigma-Aldrich Norway · Torshov · N-0401 Oslo  
**POLAND** · Sigma-Aldrich Sp. z o.o. · 61-663 Poznań **PORTUGAL** · Sigma-Aldrich Quimica, S.A. · Sintra 2710 **RUSSIA** · Sigma-Aldrich Russia · Moscow 103062 **SINGAPORE** · Sigma-Aldrich Pte. Ltd.  
**SOUTH AFRICA** · Sigma-Aldrich (pty) Ltd. · Jet Park 1459 **SPAIN** · Sigma-Aldrich Quimica, S.A. · 28100 Alcobendas, Madrid **SWEDEN** · Sigma-Aldrich Sweden AB · 135 70 Stockholm  
**SWITZERLAND** · Supelco · CH-9471 Buchs **UNITED KINGDOM** · Sigma-Aldrich Company Ltd. · Poole, Dorset BH12 4QH  
**UNITED STATES** · Supelco · Supelco Park · Bellefonte, PA 16823-0048 · Phone 800-247-6628 or 814-359-3441 · Fax 800-447-3044 or 814-359-3044 · email: [supelco@sial.com](mailto:supelco@sial.com)

Supelco is a member of the Sigma-Aldrich family. Supelco products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for a particular use. Additional terms and conditions may apply. Please see the reverse side of the invoice or packing slip.