Pentafluorobenzyl Bromide, Hexaoxacyclooctadecane

Product Specification

Pentafluorobenzyl bromide (PFBBr) converts carboxylic acids, mercaptans, phenols, and sulfonamides to halogenated derivatives that are easily detected by electron capture. Electron capturing esters are popular for GC analyses of short chain fatty acids. The reagent can be used for identification and detection of trace amounts of carboxylic acids, mercaptans, and phenols in drinking water. PFBBr is used in extractive alkylation (simultaneous extraction and derivatization), in conjunction with tetrabutylammonium hydrogen sulfate as the counterion. This procedure, also called ion-paired extraction, allows extraction/derivatization analyses of drugs from biological matrices. The analyte is removed as an ion (anion) through the use of a quaternary ammonium cation. The anion moves from the aqueous phase to the organic phase when a sample-specific pH is achieved. Once in the organic phase, the anion comes in contact with the alkylation reagent, PFBBr, and is easily derivatized.

1,4,7,10,13,16-Hexaoxacyclooctadecane (18 crown 6) is an 18-membered crown ether ring with 6 oxygen atoms. 18 crown 6 (and other crown ethers) is a phase transfer catalyst, forming complexes with many cations, particularly potassium, in nonpolar organic solvents. In the reaction of a crown ether with the potassium salt of an acid the potassium ion is complexed into the center of the ring, mainly through electrostatic forces. This makes the anionic portion of the analyte molecule very reactive to an alkyl halide, leading to alkylation under mild conditions.

PFBBr and 18 crown 6 are used in combination to prepare pentafluorobenzyl-phenol derivatives for US Environmental Protection Agency Method 604 (analyses of phenols in wastewater).

Features/Benefits

PFBBr converts carboxylic acids, mercaptans, phenols, and sulfonamides to halogenated derivatives easily monitored by electron capture. The derivatives also are detectable by UV, for HPLC and TLC applications.

Extraction alkylation with PFBBr allows simultaneous extraction and derivatization.

18 crown 6 is effective for analyses of small cations.

Typical Procedures

These procedures are intended to be guidelines and may be adapted as necessary to meet the needs of a specific application. Always take proper safety precautions when using an esterifying 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.

Acids

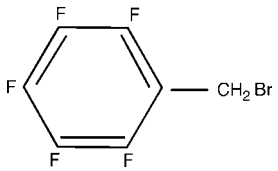
1. Combine 0.8mg acid and 100mL acetone. Add 250mg PFBBr and 50mg potassium bicarbonate.*
2. Reflux for 3 hours.
3. Add 500mL ethyl ether and 20mL ethyl acetate.
4. Wash briefly with water, then dry over sodium sulfate and evaporate to dryness.

* The crown ether confers high reactivity on the sample anion, eliminating the need for a large excess of reagent and subsequent removal of the excess before GC/ECD. Use a strong base (e.g., K_2CO_3) to derivatize both carboxylic acids and phenols; a weaker base (e.g., KOAc, $KHCO_3$, KCNO) will give selective derivatization of carboxylic acids.

Properties

Pentafluorobenzyl Bromide

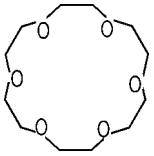
Structure:



CAS Number: 1765-40-8
Molecular Formula: $CH_6F_5CH_2Br$
Formula Weight: 260.09
bp: 174-175°C
d: 1.728
n_D: 1.4720
Appearance: clear, colorless liquid

1,4,7,10,13,16-Hexaoxacyclooctadecane

Structure:



CAS Number: 17455-13-9
Molecular Formula: $C_{12}H_{24}O_6$
Formula Weight: 264.32
mp: 42-45°C
Appearance: white solid

797-0248,0249

5. Dissolve residue in hexane containing 1% acetone and 1% ethanol.
6. Analyze 1µL aliquot by GC.

   Note: In evaporating the extract, expect some loss of the highly volatile derivatives of low molecular weight acids. Water in the reaction mixture will lead to production of artifacts.

Extractive Alkylation

1. Combine 0.2mg sample and 1mL methylene chloride in a reaction vessel.
2. Add 1mL 0.1M tetrabutylammonium hydrogen sulfate, 1mL 0.2M sodium hydroxide, and 25µL PFBBr and cap.
3. Shake for 20-30 minutes at 25°C.
4. Analyze aliquots by GC/FID.

   For GC/ECD analysis, evaporate to dryness to eliminate methylene chloride. Dissolve the residue in an appropriate solvent.

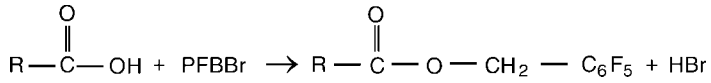
Reagent for Preparing Pentafluorobenzyl-Phenol Derivatives

Combine 1mL PFBBr and 1g 18 crown 6. Dilute with 50mL 2-propanol.

1mL of this reagent will derivatize up to 0.3mg of phenols. US EPA Method 604 describes how to add the reagent to the sample. (Obtain method from NTIS, 5285 Port Royal Road, Springfield, VA 22161 USA, Tel.: 703-487-4650; request *Methods for Chemical Analysis of Water & Waste* NTIS order no. PB 84-128-677 (March 1983).

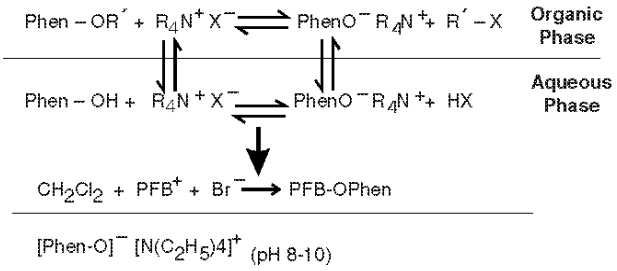
Mechanism (1,2)

Pentafluorobenzyl Bromide



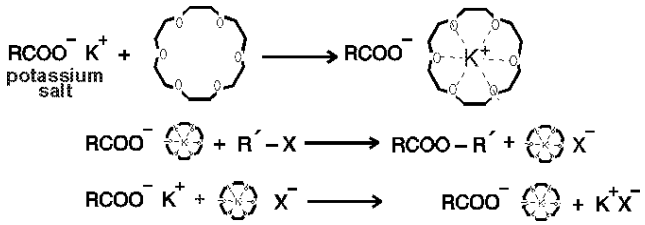
Adapted from Blau and Halket (1).

Extractive Alkylation (Phenols)



Adapted from Knapp (2).

1,4,7,10,13,16-Hexaoxacyclooctadecane



Adapted from Knapp (2).

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Derivatization times vary widely, depending upon the specific compound(s) being derivatized. 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. If derivatization is not complete under the procedure described here, the addition of a catalyst, use of another solvent, higher reaction temperature, longer reaction time, and/or higher reagent concentration should be evaluated.

Toxicity – Hazards – Storage – Stability

Pentafluorobenzyl bromide is corrosive and a lachrymator.

Hexaoxacyclooctadecane is toxic and an irritant.

Store these reagents in bottles or ampuls at room temperature, in a dry, well ventilated area. Use only in a well ventilated area. Moisture can hinder the effectiveness of these reagents.

Recommended storage conditions for the unopened product are stated on the label. 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.

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.

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.

Additional Reading

F.K. Kawahara, Anal. Chem. 40, 2073 (1968).
O. Gyllenhaal, *et al.,* J. Chromatogr. 129, 295 (1976).
H.D. Durst, *et al.,* Anal. Chem. 47, 1797 (1975).
P.T.-S. Pei, *et al.,* Lipids 11, 814 (1976).
B. Davis, Anal. Chem. 49, 832 (1977).

Ordering Information

Description	Cat. No.
PFBBr	
5g	**33001**
Hexaoxacyclooctadecane	
25g	**33003-U**
Microreaction Vessels with Hole Caps and Septa	
1mL, pk. of 12	**33293**
3mL, pk. of 12	**33297**
5mL, pk. of 12	**33299**
Books	
Handbook of Derivatives for Chromatography	
K. Blau and J. Halket	**Z246220**
Handbook of Analytical Derivatization Reactions	
D.R. Knapp	**23561**