

Bismuth Pentafluoride



[7787-62-4] BiF₅ (MW 303.97)

InChI = 1/Bi.5FH/h;5*1H/q+5;;;;;p-5/fBi.5F/h;5*1h/qm;
5*-1/rBiF5/c2-1(3,4,5)6

InChIKey = BAHXPLXDFQOVHO-LBOISHKDCH

(strong Lewis acid, oxidant, and fluorinating agent. Catalyst for carbocation formation. Used in the manufacture of gasoline blends, iodofluorination of fluoroolefins, and the preparation of fluoroalkylphosphoranes)

Alternative Names: bismuth(V) fluoride, bismuth fluoride.

*Physical Data:*¹ white crystalline solid (tetragonal needles); mp 151.4 °C; bp 230 °C; *d*²⁵ 5.52.

Solubility:^{1a,2} slightly soluble in many organic and inorganic solvents, including HF.

Preparation: bismuth pentafluoride is generally prepared by heating bismuth trifluoride with F₂ or ClF₃.³⁻⁵

Purification: bismuth pentafluoride can be purified by sublimation under vacuum at around 100 °C in an apparatus made entirely of Vycor glass, which is not attacked by bismuth pentafluoride.³ Bismuth pentafluoride can also be crystallized from anhydrous HF prior to use.⁶

*Spectroscopic Data:*⁵ (IR) 625, 580, and 450 cm⁻¹; (Raman) 597, 571, and 256 cm⁻¹.

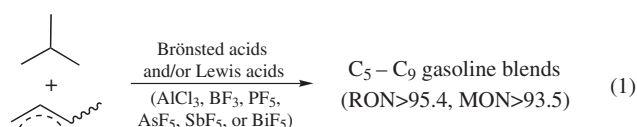
Handling, Storage, and Precautions: bismuth pentafluoride is moisture sensitive. It should be stored in a tightly closed container and kept in a dry environment. Bismuth pentafluoride may cause irritation of the eyes, skin, digestive tract, and respiratory tract. The toxicological properties of bismuth pentafluoride have not been fully investigated.

General. Bismuth pentafluoride is known as a powerful fluorinating and oxidizing agent. The physical properties and structure of bismuth pentafluoride have been probed by both experiments and theoretical calculations. Several groups have also described the inorganic chemistry of BiF₅.⁷

There are few reports of bismuth pentafluoride as a reagent for organic synthesis. Bismuth pentafluoride is considered a Lewis superacid that is stronger than anhydrous aluminum trichloride (the most commonly used Friedel–Crafts Lewis acid). It is often listed among the employable catalysts for Lewis-acid-mediated reactions,⁸⁻¹⁰ but specific examples and details of its actual use are very rare.¹⁰ Indeed, the substitution of bismuth pentafluoride for other Lewis acids should be done with caution as bismuth pentafluoride tends to react explosively with organic compounds.¹¹ Likewise, bismuth pentafluoride reacts rapidly with water. This property can be put to use by employing bismuth pentafluoride as a drying agent. For example, after HF has been predried by treatment with 20 atm of F₂ at room temperature, it is often stored over bismuth pentafluoride to remove the last traces of water.¹²

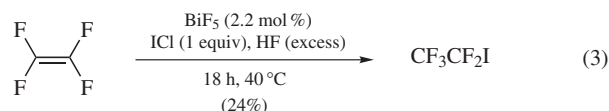
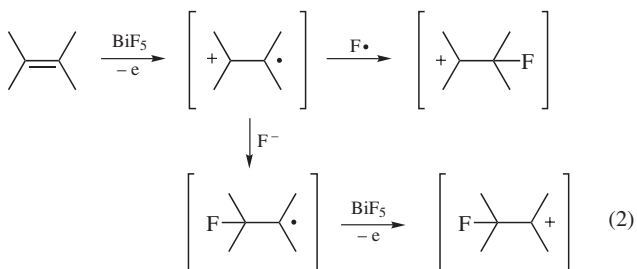
Generation and Reaction of Carbocations.

Alkylation of Aromatic Hydrocarbons or Isoparaffin with Olefins. As a solid Lewis superacid, bismuth pentafluoride is claimed as a reagent for the generation and reaction of carbocations. Again, actual detailed descriptions of how and when BiF₅ has been used in such reactions are rare. That said, bismuth pentafluoride has been reported to be analogous to antimony pentafluoride as a cocatalyst for the Lewis superacid mediated alkylation of isobutane with a mixture of 1- and 2-butenes. Under such conditions, the alkylations exhibit increased selectivity toward gasoline blends with a high research octane number (RON) and motor octane number (MON) (in practice the octane of a gasoline is reported as the average of RON and MON or R+ M/2) (eq 1).⁸ Improved stability of the solid acid catalysts, including bismuth pentafluoride, is also claimed.



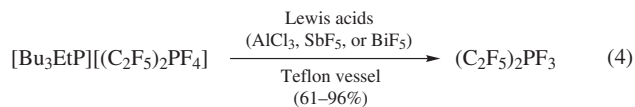
Generation of Polyfluorinated Carbocations. As a strong fluorooxidizer, the reaction of bismuth pentafluoride with olefins is said to provide for the indirect generation of fluorinated carbocations (eq 2).^{1a} The mechanism of such processes remains a subject of investigation, but appears to be dependant upon both the substrate and the fluorooxidizer. This process is likely involved in the reaction of bismuth pentafluoride with polyacetylene films, which causes the films to be doped to the metallic state, albeit with a minimal increase in their conductivity.¹³

Iodofluorination of Fluoroolefins. Another application of the above process is in the iodofluorination of fluoroolefins. In the presence of catalytic amounts of bismuth pentafluoride, tetrafluoroethylene was treated with ICl in anhydrous HF to afford pentafluoroethyl iodide. Pentafluoroethyl iodide is one of the perfluoroalkyl iodides that are used as telogens for the telomerization of tetrafluoroethylene to long-chain perfluoroalkyl iodides (eq 3).¹⁰

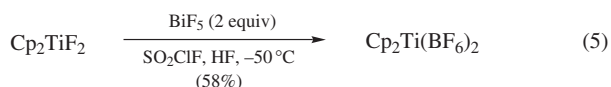


Other Reactions.

Preparation of (Fluoroalkyl)_nphosphoranes (n = 1 or 2). (Perfluoroalkyl)phosphorus(V) compounds have been studied because of their potential to serve as electrolytes in fuel cells.¹⁴ Bis(pentafluoroethyl)trifluorophosphorane, one of the (perfluoroalkyl)phosphorus(V) compounds, was prepared in high yield by the reaction of tributylethylphosphonium bis(pentafluoroethyl)tetrafluorophosphate with anhydrous HF in the presence of Lewis acids such as aluminum trichloride and antimony pentafluoride (eq 4).⁹ Here too it is claimed that the catalytic activity of bismuth pentafluoride is comparable to antimony pentafluoride.



Preparation of Fluorine Coordinated Metallocenes. Bismuth pentafluoride was reacted with Cp₂TiF₂ in SO₂ClF and HF to afford Cp₂Ti(BF₆)₂ (eq 5), the first reported fluorine-coordinated hexafluorobismuthate complex.¹⁵ The utility of the product metallocene in the service of organic synthesis was not described.



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