

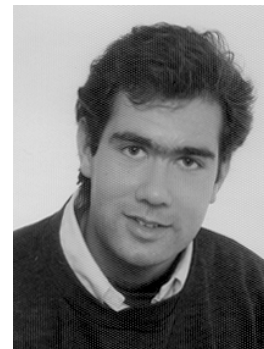
# SYNLETT Spotlight 10

## Bis(pyridine)iodonium(I)tetrafluoroborate

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Kilian Muñiz studied Chemistry at the Universität Hannover/Germany, at the Imperial College London/UK and at Universidad de Oviedo/Spain. From 1996-1998 he worked on his PhD in the group of Professor C. Bolm at the RWTH Aachen/Germany. Currently, he is carrying out postdoctoral research in the group of Professor R. Noyori at Nagoya University/Japan.



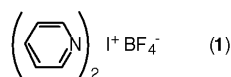
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Bis(pyridine)iodonium(I)tetrafluoroborate (**1**) - Barluenga's reagent - is a powerful iodination agent which is the reagent of choice for highly selective electrophilic iodination under mild conditions. Examples include all kinds of unsaturated substrates such as isolated and conjugated olefins,<sup>1</sup> acetylenes<sup>2</sup> and aromatic compounds<sup>3</sup> tolerating a variety of functional groups. Compound **1** also allows to control polyiodination reactions<sup>3b</sup> in a regioselective manner and has been reported to initiate iodination/cyclisation cascade-processes.<sup>4</sup>

### Preparation<sup>1a,2</sup>

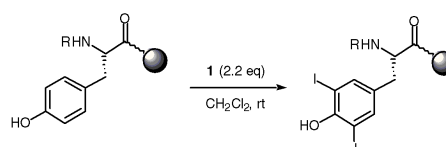
Reagent **1** is conveniently prepared by reaction of HgO/HBF<sub>4</sub>-SiO<sub>2</sub> with iodine and pyridine in CH<sub>2</sub>Cl<sub>2</sub>. After filtra-

tion of the crude reaction mixture, the title compound is precipitated by addition of cold Et<sub>2</sub>O. Further purification can be carried out by recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub>. Thereby, **1** is obtained as a white solid and should be stored under an inert atmosphere at 4°C in the dark. Generally, HBF<sub>4</sub> is added to the reaction mixture in order to release the free iodonium ion by protonation of the pyridine groups and thus preventing a possible nucleophilic reaction by the free pyridine. Alternatively, HBF<sub>4</sub> can be replaced by BF<sub>3</sub>-Et<sub>2</sub>O or CF<sub>3</sub>SO<sub>3</sub>H.

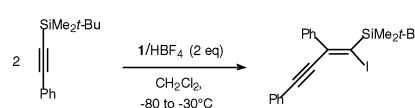


### Abstracts

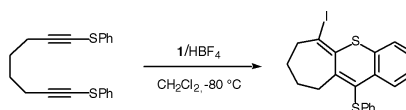
Among the many examples of reactions on aromatic systems,<sup>3</sup> **1** has recently been employed for the iodination of bioactive peptides containing Tyr. The mildness of the reagent allowed the reaction to be carried out even on solid support. Several *N*-protecting groups were tolerated and the iodination process was reported to be completely chemoselective in the presence of other aromatic groups.<sup>5</sup>



Dimerisation of silyl protected 2-aryl-alkynes was accomplished yielding the respective enynes in high yields and with exclusive (*Z*)-configuration. These products were shown to be either suitable starting materials for endiynes cores or, upon further treatment with **1**, they rearranged into (*E*)-1,2-diiodo-1,3-butenynes in a stereoselective manner.<sup>6</sup>



In the presence of **1**/HBF<sub>4</sub> propargylic thioethers undergo a novel intramolecular *exo-endo*-cyclisation. This sequence represents a novel domino reaction which involves an alkyne-alkyne coupling followed by an intramolecular Friedel-Crafts like cyclisation.<sup>7</sup>



### References

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