SYNLETT Spotlight 10

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

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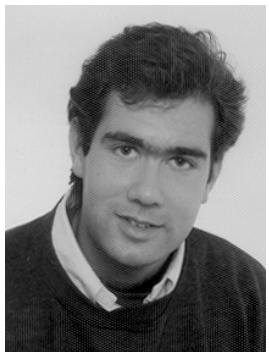
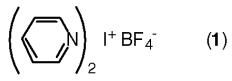


Bis(pyridine)iodonium(I)tetrafluoroborate (**1**) - Barluenga's reagent - is a powerful iodination agent which is the reagent of choice for highly selective electrophilic iodination under mild conditions. Examples include all kinds of unsaturated substrates such as isolated and conjugated olefins,[1]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

Preparation[1a,2]

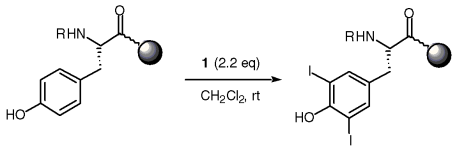
Reagent **1** is conveniently prepared by reaction of HgO/HBF_4-SiO_2 with iodine and pyridine in CH_2Cl_2. After filtration of the crude reaction mixture, the title compound is precipitated by addition of cold Et_2O. Further purification can be carried out by recrystallisation from CH_2Cl_2/$CHCl_3$. Thereby, **1** is obtained as a white solid and should be stored under an inert atmosphere at 4°C in the dark. Generally, HBF_4 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_4 can be replaced by BF_3-Et_2O or CF_3SO_3H.



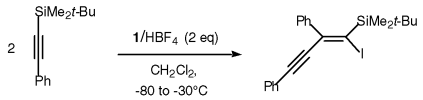
(**1**)

Abstracts

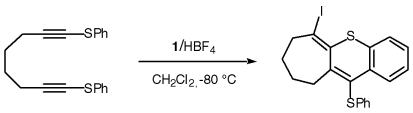
Among the many examples of reactions on aromatic systems,[3] **1** has recently been employed for the iodination of bioactive peptides containing Tyr. The mildness of the reagent allowed the reaction to be carried out even on solid support. Several *N*-protecting groups were tolerated and the iodination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



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 endiyne cores or, upon further treatment with **1**, they rearranged into (*E*)-1,2-diiodo-1,3-butenynes in a stereoselective manner.[6]



In the presence of **1**/HBF_4 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.[7]



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