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 acetylenes² and aromatic compounds³ 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/HBF₄-SiO₂ with iodine and pyridine in CH₂Cl₂. After filtra-

tion of the crude reaction mixture, the title compound is precipitated by addition of cold Et₂O. Further purification can be carried out by recrystallisation from CH₂Cl₂/CHCl₃. Thereby, **1** is obtained as a white solid and should be stored under an inert atmosphere at 4°C in the dark. Generally, HBF₄ 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, HBF₄ can be replaced by BF₃-Et₂O or CF₃SO₃H.

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 endiynes 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**/HBF₄ 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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Article Identifier:

1437-2096,E;1999,0,10,1679,1679,ftx,en;V01299ST.pdf