

SYNLETT Spotlight 177

Phenyliodine(III) Bis(trifluoroacetate) (PIFA)

Compiled by Xiao-Yu Han



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

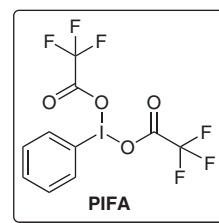
Xiao-Yu Han was born in Lingshi, Shanxi Province (P. R. of China) in 1981. She received her Bachelor of Science at Datong University. Presently she is working as a postgraduate at Suzhou (Soochow) University, in the College of Chemistry and Chemical Engineering, under the supervision of Professor Ya-Hong Li. Her research field is mainly focused on the new synthetic approaches catalyzed by titanium complexes.

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Introduction

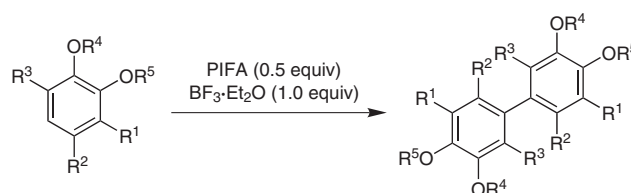
Hypervalent iodine(III) reagents are now extensively used in organic synthesis.¹ In particular, phenyliodine(III) bis(trifluoroacetate) (PIFA) has received a lot of attention due to its low toxicity, ready availability, easy handling, and reactivity similar to that of heavy-metal reagents or anodic oxidation. Regarding the oxidation of phenol derivatives with PIFA, in most cases, the reaction proceeds via the intermediate in which the phenolic oxygen reacts with the iodine center of the hypervalent iodine reagent, followed by the nucleophilic attack of the alcohol,² alkene,³ amide,⁴ carboxylic acid,⁵ oxime,⁶ fluoride ion,⁷

water⁸ or electron-rich aromatic ring⁹ to give the cross-conjugated cyclohexadienone either via an inter- or an intramolecular reaction pathway.

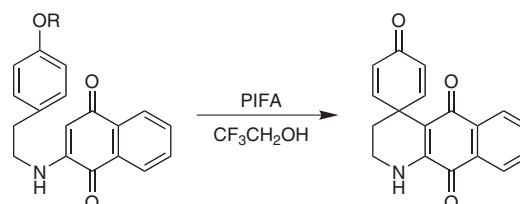


Abstracts

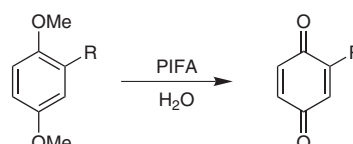
(A) Hirofumi et al.¹⁰ reported that multiple iodinated biaryls can be prepared in yields up to 75% by direct oxidative coupling reaction of the iodinated arenes. The PIFA-mediated dehydrodimerization is superior to all other known methods. The developed protocol is reliable and easy to perform.



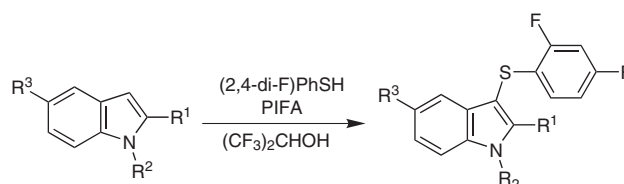
(B) The hypervalent iodine oxidation of phenol derivatives bearing aminoquinones at the *ortho* or *meta* positions in 2,2,2-trifluoroethanol was investigated with the aim of preparing novel antitumor compounds. Azacarbo-cyclic spirodienone derivatives or phenol derivatives containing the 2,3-dihydro-1*H*-azepine system were selectively obtained by the reaction of these phenol derivatives and the hypervalent iodine reagent PIFA.¹¹



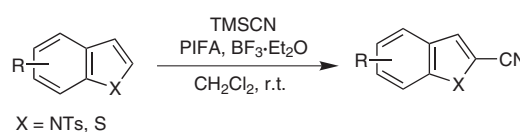
(C) A new method for preparing 4-quinone derivatives from phenol ether derivatives in water using PIFA was developed. The presented reaction proceeds in good to excellent yields under mild reaction conditions.¹²



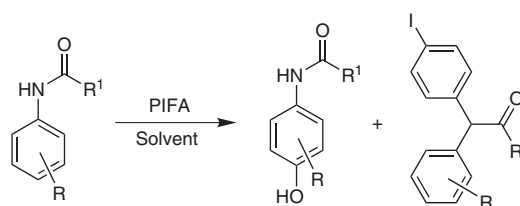
(D) The direct 3-arythiolation of 2-substituted indoles using PIFA in $(\text{CF}_3)_2\text{CHOH}$ with a wide variety of benzenethiols has been accomplished. This result was consistent with a proposed mechanism involving benzenethiol displacement of an intermediate 3-IPh indole complex.¹³



(E) PIFA mediates the selective cyanation reactions of a wide range of electron-rich heteroaromatic compounds such as pyrroles, thiophenes, and indoles under mild conditions. These reactions proceed via a cationic radical intermediate, and the successful transformation presumably depends on the oxidation–reduction potential of the substrates used.¹⁴



(F) The reaction of anilides with phenyliodine(III) bis(trifluoroacetate) (PIFA) in trifluoroacetic acid (TFA) is described. When the acyl group of the anilide is highly electronegative, such as trifluoroacetyl, or the phenyl group is substituted with an electron-withdrawing group, the 4-iodophenyl group is transferred from PIFA to the amide nitrogen to afford acetyldiarylamines. On the other hand, when the acyl group contains an electron-donating moiety, such as 4-methoxyphenyl, or the phenyl group is substituted with an electron-donating functional group, a trifluoroacetoxy ring is transferred to the *para* position of the anilide aromatic ring. This group is hydrolyzed during workup to produce the corresponding phenol.¹⁵



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