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IPy_2BF_4 is Also a Useful Reagent for Stereospecific Iodine-Silicon Exchange in Open Chain Trimethylsilylalkenes

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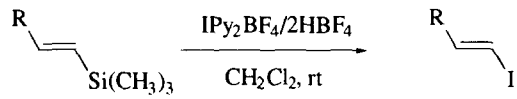
Abstract: Reaction of the title monosubstituted vinylsilanes with IPy_2BF_4/HBF_4 gives iodoalkenes through the ipso-substitution process with stereospecific retention of configuration.

The reaction of electrophiles towards vinylsilanes gives addition or, more frequently, substitution products with remarkable regio- and stereoselectivity.[1] The ability for silicon to stabilize an electron deficiency onto the β-carbon accounts well for the observed regioselectivity.[2,3] Moreover, for the ipso-substitution, stereospecific retention of configuration occurs for the reaction with protons[4] and acyl cations;[5] nevertheless, this is not so general for halogens.[1] For bromine both retention[6] and inversion[5,7] take place depending on the nature of the substituents. Similarly, for iodine, retention of configuration is the common result for 1,2-dialkylsubstituted vinylsilanes[5] or open chain (*Z*)-monosubstituted vinylsilanes,[7a,8] whereas inversion happens starting from the (*E*) isomer.[8] The feasibility of a two step approach, starting from ICl addition followed by desilicochlorination with base, was explored in an attempt to synthesize (*E*)-1-iodoalkenes by means of silicon-iodine exchange.[8,9] Overall inversion of configuration was observed, but the process is of limited synthetic interest to prepare pure (*E*)-1-iodoalkenes.[8,9] More recently, both the use of iodine with added amounts of Lewis acid, the so called "tunable stereoselective iododesilylation" of alkenyltrimethylsilanes,[10] and the modification of the substituents onto silicon[11] have proven useful for this purpose.

In this letter we report the reaction of open chain monosubstituted trimethylsilylalkenes with IPy_2BF_4.[12] It is known that reaction of IPy_2BF_4 with 2 equivalents of HBF_4 in CH_2Cl_2 provides an efficient method to accomplish the iodofunctionalization of unsaturated systems; this method takes advantage of the low nucleophilicity of the BF_4^- counteranion that allows the reaction of the intermediate iodonium ion with several nucleophiles.[13] Besides, the counteranion acts as a source of fluoride in the absence of other nucleophiles.[13c]

In keeping with the widely accepted mechanism to account for the ipso-substitution by iodine[14] retention of configuration is attributed to rapid elimination of the trimethylsilyl group (TMS) from the intermediate carbenium ion prior to its capture by nucleophiles.[15] On this basis, it was challenging to test open chain monosubstituted trimethylsilylalkenes towards IPy_2BF_4 and check whether this electrophilic source of iodine would be suitable to iodinate the above mentioned silanes with stereospecific retention of configuration.

Initially, we examined the behaviour of the (*E*)-isomers as starting materials (Scheme 1). The reaction takes place by dissolving IPy_2BF_4 in CH_2Cl_2 under nitrogen (3 mL of solvent were used for each mmol of the iodonium salt), when the mixture is homogeneous HBF_4 is added (2:1, with respect to the iodinating reagent, except for **6**, 1:1 in this case),[16] inmediately, the formation of a precipitate is observed while the colour of the solution become deep red. Addition of the silane (**1-6**, equimolar amount with IPy_2BF_4) leads to its instantaneous conversion into the related iodoalkene (**7-12**). Hydrolysis, extraction and removal of solvents affords crude reaction mixtures; ^1H NMR clearly shows that silicon-iodine exchange has taken place with full retention of configuration.

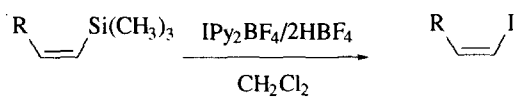


(**1- 6**)	(**7- 12**)
1 (R: cyclohexyl)	**7** (78%)
2 (R: 4-Cl-C_6H_4)	**8** (75%)
3 (R: C_6H_5)	**9** (80%)
4 (R: 2-naphthyl)	**10** (89%)
5 (R: 4-CH_3-C_6H_4)	**11** (97%)
6 (R: 4-CH_3O-C_6H_4)	**12** (99%)

Scheme 1

The iodoalkenes were purified by column chromatography (silica gel, hexane: ethyl acetate, 40:1) or distillation under vacuum of the Kugelrohr type (for **7** and **9**). Structures were assigned on the basis of their NMR, IR and MS data and the yields, calculated from pure isolated compounds, are referred to the silane. This reaction can be successfully used for multigram quantities.

In a related process, (*Z*)-isomers of the starting vinylsilane give stereospecifically the corresponding (Z)-iodoalkenes (Scheme 2).



(**13 - 18**)	(**19 - 24**)
13 (R: n-hexyl)	**19** (77%)
14 (R: cyclohexyl)	**20** (85%)
15 (R: 4-Cl-C_6H_4)	**21** (78%)
16 (R: C_6H_5)	**22** (82%)
17 (R: 2-naphthyl)	**23** (92%)
18 (R: 4-CH_3-C_6H_4)	**24** (97%)

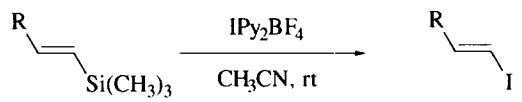
Scheme 2

Several modifications of the aforementioned protocol should be taken into account to optimize the reaction

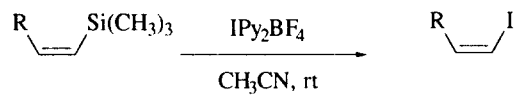
for this series. Although stereospecific silicon-iodine exchange still takes place at room temperature for alkyl-substituted silanes (**13-14**), the stereoselectivity significantly decreases for the aryl-substituted ones (**15-18**). In this case, by simply lowering the temperature at -60 °C stereospecific retention of configuration can also be achieved. Monitoring for the reaction by TLC reveals 90 minutes to be the time required to achieve conversions in the range of those at room temperature. Throughout the reaction, temperature is stabilized at -60 °C; an additional modification concerns the amount of solvent, that should be increased to 5mL for each mmol of IPy_2BF_4.

In summary, the results depicted in Schemes 1 and 2 clearly prove that silicon-iodine exchange in open-chain monosubstituted alkenes can now be carry out efficiently and stereospecifically by reaction with IPy_2BF_4, irrespectively of the configuration of the starting silane.

Another aspect of this reaction we have looked into is the influence of the solvent. In this regard we have found that acetonitrile is also appropriate, avoiding the need of acid treatment for IPy_2BF_4 to induce silicon-iodine exchange. Nevertheless, the synthetic usefulness of these alternative conditions is limited depending on the substitution pattern in the starting silane. Thus, for the aryl-substituted vinylsilanes, acetonitrile provides an excellent alternative to accomplish the silicon-iodine exchange in high yield, under neutral conditions (Scheme 3). However, for the alkyl-substituted ones, the reaction fails to furnish good yield of the iodoalkenes ; under these conditions, addition products of both pyridine and acetonitrile (in a Ritter-type process) compete with those derived from silicon-iodine exchange.



2 (R: 4-Cl-C_6H_4) **8** (80%)
3 (R: C_6H_5) **9** (83%)
5 (R: 4-CH_3-C_6H_4) **11** (85%)
6 (R: 4-CH_3O-C_6H_4) **12** (80%)



15(R: 4-Cl-C_6H_4) **21** (83%)
16(R: C_6H_5) **22** (80%)
18(R: 4-CH_3-C_6H_4) **24** (85%)

Scheme 3

Only 1mL of acetonitrile for each mmol of IPy_2BF_4 is required in this procedure and the reaction takes place in an open flask (up to the 5 mmol scale a simple test tube will be adequate). After addition of the silane, instantaneous change of colour and evolution of heat are noticed. Hydrolysis and conventional work up provides minor amounts of addition products and the corresponding iodoalkene, easily separated by selective solubilization. Remarkably, this procedure gives always retention at room temperature, even for the (Z)-isomers. Increasing the amount of solvent to 5 mL/mmol IPy_2BF_4 results in partial inversion.

In short, new methods have been established for the stereospecific silicon-iodine exchange starting from open chain monosubstituted trimethylsilylalkenes.

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15 To account for the retention of configuration, TMS-group elimination is intended taking place by nucleophilic attack on silicon from the conformation where the silyl group stabilization of the β-carbenium ion competes well with the iodonium bridge in equilibrium (see reference 14 in this letter).

16 A 54% ethereal solution, commercially available from Merck.

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