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A simple and versatile method for the hydroiodination of alkenes and alkynes using I_2 and Et_3SiH in the presence of copper(II)

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Abstract—The reagent system $CuO·HBF_4/I_2/Et_3SiH$ generates in situ hydrogen iodide which regioselectively adds to alkenes and alkynes. The mild nature of this system tolerates the presence of different groups on the unsaturated compound. © 2002 Elsevier Science Ltd. All rights reserved.

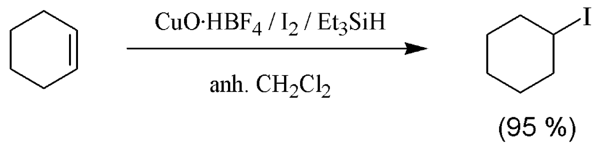
The classical synthesis of alkyl iodides from alkenes and hydrogen iodide often leads to low yields and side reactions due to uncontrollable iodine liberation.[1] Consequently, several alternative approaches to hydroiodination have been developed:[2] chlorotrimethyl silane/sodium iodide/water,[3] iodine/alumina,[4] borane-*N*,*N*-diethylaniline complex/iodine/acetic acid,[5] iodotrimethyl silane/alumina[6] and aluminium triiodide/water.[7] However, the use of iodotrimethylsilane (or its precursor) does not tolerate groups such as ester or acetals,[8] and other reagents are not easy to manipulate.

We have previously reported the iodofunctionalization of different unsaturated systems with a mixture of iodine and a solution of $CuO·HBF_4$ (which resulted from admixture of copper(II) oxide and aqueous tetrafluoroboric acid) in the presence of nucleophiles.[9,10] The sole example described using triethylsilane as reagent leads to the hydroiodination of cyclohexene in excellent yield (Scheme 1) but the usefulness of this procedure to obtain alkyl iodides is far from having been sufficiently explored. Since all reagents are commercially available and can be manipulated without any special caution, we found it of interest to investigate this addition reaction with a range of alkenes and alkynes. We report here our results in this field.

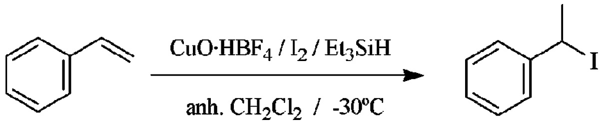
Treatment of styrene with a dehydrated suspension[11] of $CuO·HBF_4$ and iodine in anhydrous CH_2Cl_2 afforded 1-iodo-1-phenylethane as the main product.[12] In order to establish an optimum condition for hydroiodination, the addition was carried out under several reaction conditions. The highest yield was obtained by stirring the mixture at −30°C for 3 h (Scheme 2 and Table 1).

The regioisomer obtained corresponds to a Markovnikov addition of hydrogen iodide, which indicates that this reagent should be generated in situ in the course of the reaction from I^+ and Et_3SiH. This hypothesis was confirmed when we performed the reaction using ethyl acrylate as the starting alkene, under the same experimental conditions, since ethyl 3-iodopropionate was formed (Table 1, entry 2).[13] The latter result also indicates that our method tolerates an ester group, which could be also verified using 4-acetoxystyrene (entry 3).

To check whether the reagent system could be used for halogen-containing products, *p*-chlorostyrene was treated with $CuO·HBF_4/I_2/Et_3SiH$, giving 1-iodo-1-(*p*-chlorophenyl)ethane in 61% yield (entry 4).



Scheme 1.



Scheme 2.

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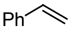
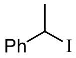
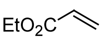
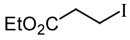
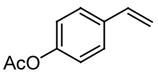
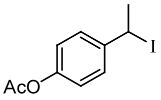
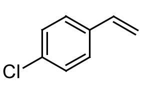
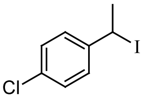
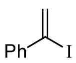
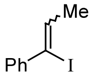
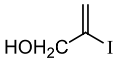
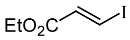
Table 1. Reaction of $CuO\cdot HBF_4/I_2/Et_3SiH$ to alkenes and alkynes[a]

Entry	Substrate	Product	Yield %[b]
1			65
2			52
3			80
4			61
5	Ph−C≡C−H		43
6	Ph−C≡C−Me		52[c]
7	HOH_2C−C≡C−H		55
8	EtO_2C−C≡C−H		70

[a] Reaction conditions: CuO (4 mmol), HBF_4 (8 mmol), I_2 (6 mmol), Et_3SiH (24 mmol), unsaturated system (8 mmol), anhydrous CH_2Cl_2 (20 ml) -30°C, 3 h, under argon.

[b] All compounds were purified by chromatography (silica gel: hexane). Yields are for pure isolated products, relative to alkene or alkyne and show spectral data and elemental analyses in accordance with the given structures.

[c] Obtained as a mixture of (*E*)- and (*Z*)-isomers in 65:35 ratio, determined by ^1H NMR spectra of the crude reaction.

Next, we investigated the addition of hydrogen iodide to a number of alkynes. The results are also summarized in Table 1. We found that the procedure afforded α-iodostyrene, resulting from a mono hydroiodination of phenylacetylene (entry 5). In a similar reaction, 1-phenyl-1-propyne gave a mixture of (*E*)- and (*Z*)-1-iodo-1-phenyl-1-propene (65 and 35%, respectively, entry 6). These α-iodostyrenes are relevant reagents in organic synthesis.[14] The reaction with propargyl alcohol (entry 7) and ethyl propiolate (entry 8) illustrates other examples of the mildness of the reaction.

In conclusion, we have developed a mild method for the regioselective hydroiodination of alkenes and alkynes based on common reagents. Further studies to extend the scope of this reaction are in progress.

Acknowledgements

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10. We have also reported one example of hydroiodination with IPy_2BF_4: Barluenga, J.; González, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 319.
11. The aqueous solution of $CuO\cdot HBF_4$ was evaporated at reduced pressure (10^{-2} mmHg and 50–60°C) to constant weight (see Ref. 9). To avoid the water of crystallization present in copper(II) tetrafluoroborate, silica gel can be added prior to dryness.
12. Some polymeric material was obtained and the product needed to be purified by column chromatography on silica gel.
13. Comparing the regiochemistry obtained for the reactions with styrene and ethyl acrylate, a mechanism involving a radical addition can be discarded.
14. For a recent application, see: Chan, P. W. H.; Kamijo, S.; Yamamoto, Y. *Synlett* **2001**, 910.