Tetrahedron Letters, Vol.31, No.19, pp 2751-2754, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

SYNTHESIS OF 2-FUNCTIONALIZED 1-CHLORO-1-IODO-1-ALKENES FROM 1-CHLORO-1-ALKYNES AND IPy_2BF_4

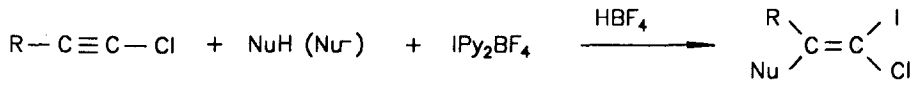
José Barluenga,* Miguel A. Rodríguez, and Pedro J. Campos

Departamento de Química Organometálica, Facultad de Química,
Universidad de Oviedo, 33071-Oviedo, Spain

Abstract: 1-Chloro-1-alkynes react with bis(pyridine)iodine(I)tetrafluoroborate (**1**) and nucleophiles (AcOH, HCOOH, Cl, Br, I) to give, in a regio- and stereoselective addition, 2-functionalized 1-chloro-1-iodo-1-alkenes.

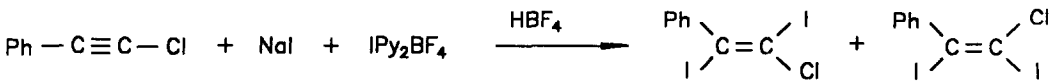
Vinyl iodides have been of interest in recent years due to their versatility in organic synthesis[1] and photochemistry,[2] and because they can be transformed in the presence of less reactives vinyl halides.[1a,3] In this way, chloroiodoalkenes presents a high importance to carry out these kind of processes. Some procedures have been described to prepare 1-chloro-1-iodo-1-alkenes but the scope is very limited: the addition of hydrogen chloride to iodopropiolic acid yields the two stereoisomers in equimolecular amounts,[4] the exchange reaction between 1,1-dichloro-1-alkenes and sodium iodide is achieved in dichlorovinylethyl sulfone[5] but, in general, vinyl chlorides are unsatisfactory substrates because of their reluctance towards exchange,[6] and finally, the halogen addition to chloroacetylenes, but this process often leads to the diaddition products.[7]

We have recently described the iodofunctionalization of alkynes with bis(pyridine)iodine(I) tetrafluoroborate (**1**) as an electrophilic reagent.[8,9] We now report the electrophilic addition of 1 to 1-chloro-1-alkynes,[10] in the presence of two equivalents of tetrafluoroboric acid and different nucleophiles, to obtain 2-functionalized 1-chloro-1-iodo-1-alkenes. The reaction occurs at room temperature in good to moderate yields (see Table) with the formation of a single stereoisomer (see Scheme 1) except for 1-chloro-2-phenylethyne and sodium iodide as nucleophile in which a mixture of stereoisomers is observed (see Scheme 2).



R = Ph	Nu =	OAc	2	R = ^{n}Hex	Nu =	OAc	6
		OCHO	3			OCHO	7
		Cl	4			Cl	8
		Br	5			Br	9
						I	10

Scheme 1



11 **12**

Scheme 2

The reactions are clean, and after usual work-up procedure the reaction products were purified by washing with hexane in a short column packed with silica to eliminate the unreacted starting alkyne (g.c. purity > 95%).[11] 1-Chloro-1-iodo-1-alkenes show ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry in accordance with the proposed structures.

In most cases, only a single stereoisomer was observed, probably the E isomer, which is in agreement with the previously proposed mechanism through a vinyleneiodonium ion.[8b] In addition, when the steric hindrance of the alkyne substituent was increased (R = Ph), some *syn*-addition occured with the strongest nucleophile (I^-) and a mixture of stereoisomers (**11** and **12**) were formed.

Our method allows the preparation of several 1-chloro-1-iodo-1-alkenes with a function in the 2-position. Furthermore, the products **5** and **9** contain three different halogens with well-defined stereochemistry.

Acknowledgements: The present work was financed by CAYCIT. One of us (M.A.R.) acknowledges a grant by the Ministerio de Educación y Ciencia.

Table: Iodofunctionalization of 1-chloro-1-alkynes with **1**

Product	Nucleophile	Solvent	Time (h)	Yield (%)[a]
2	AcOH	$AcOH/CH_2Cl_2$ (2:1)	14	75
3	HCOOH[b]	$HCOOH/CH_2Cl_2$ (2:1)	14	90
4	LiCl[c]	$MeCN/H_2O$ (5:1)	80	60
5	LiBr[c]	$MeCN/H_2O$ (5:1)	70	57
6	AcOH	$AcOH/CH_2Cl_2$ (2:1)	14	63
7	HCOOH[b]	$HCOOH/CH_2Cl_2$ (2:1)	14	59
8	LiCl[c]	$MeCN/H_2O$ (5:1)	80	54
9	LiBr[c]	$MeCN/H_2O$ (5:1)	70	51
10	NaI[c]	$MeCN/H_2O$ (5:1)	30	35
11/12[d]	NaI[c]	$MeCN/H_2O$ (5:1)	20	42 (4.5/1)[e]

[a]Yield of isolated products, relative to starting **1** and not optimized. [b]Aqueous 85% solution. [c]Mole ratio Nu:**1** = 10:1. [d]E- and Z- isomers could not be separated. [e]Isomer ratio, determined by ^{13}C NMR spectra of the crude reaction.

REFERENCES AND NOTES

1.- See, for example: (a) E. Negishi: *Organometallics in Organic Synthesis*, J. Wiley, New York, 1980, p. 30; (b) G.H. Posner: *An Introduction to Synthesis Using Organocopper Reagents*, R.E. Krieger, Malabor, Florida, 1988, p. 72; (c) M. Hanack, *Angew. Chem. Int. Ed. Engl.*, **17**, 333 (1978); (d) E. Negishi, L.F. Valente, and M. Kobayashi, *J. Am. Chem. Soc.*, **102**, 3298 (1980); (e) P.J. Kropp, *Acc. Chem. Res.*, **17**, 131 (1984).

2.- P.J. Kropp, S.A. McNeely, and R.D. Davis, *J. Am. Chem. Soc.*, **105**, 6907 (1983).

3.- E. Negishi, N. Okukado, L.F. Lovich, and F. Luo, *J. Org. Chem.*, **49**, 2629 (1984); F. Tellier, R. Sauvêtre and J. Normant, *Tetrahedron Lett.*, **27**, 3147 (1986).

4.- K. Andersson, *Chem. Scripta*, **2**, 117 (1972).

5.- B.A. Shainyan, and A.N. Mirskowa, *Zh. Org. Khim.*, **19**, 1146 (1983).

6.- H. Suzuki, M. Aihara, H. Yamamoto, and Y. Tamamoto, T. Ogawa, *Synthesis*, 237 (1988).

7.- S.Y. Delavarenne, and H.G. Viehe in: *The Chemistry of Acetylenes*, M. Dekker, New York, 1969, Cap 10, p. 699.

8.- (a) J. Barluenga, M.A. Rodríguez, J.M. González, P.J: Campos, and G. Asensio, *Tetrahedron Lett.*, **27**, 3303 (1986); (b) J. Barluenga, M.A. Rodríguez, and P.J. Campos, *J. Org. Chem.*, in the press.

9.- J. Barluenga, M.A. Rodríguez, P.J. Campos, and G. Asensio, *J. Am. Chem. Soc.*, **110**, 5567 (1988); J. Barluenga, M.A. Rodríguez, P.J. Campos, *J. Chem. Soc., Perkin Trans. 1*, sended to publish.

10.- The previously described method to prepare 1-chloro-1-alkynes[12] is not general. We have prepared the starting chloroalkynes by the follow procedure: To a solution of the corresponding terminal alkyne (8 mmol) in dry tetrahydrofuran (40 ml) was added $LiAlH_4$ (2.4 mmol, 2.40 ml of 1 M solution in THF) at room temperature under inert atmosphere. After stirring one hour, N-chlorosuccinimide (8 mmol, 1.07 g) was added and 30 minutes later, the solution was hydrolized with water (50 ml), and extracted with methylene dichloride (3 x 50 ml), dried over Na_2SO_4 and evaporated in vacuo. Reaction products were purified by distillation.

11.- Typical procedures for iodofunctionalization of 1-chloro-1-alkynes: To a solution of the nucleophile in the appropiate solvent (15 ml) (see Table), HBF_4 (10 mmol, 1.40 ml of ethereal 54% solution), **1** (5 mmol, 1.86 g), and the corresponding chloroalkyne (5 mmol) were added at room temperature. After stirring, the red solution was hydrolized with water (50 ml), extracted with CH_2Cl_2 (3 x 25 ml), washed with 5% aqueous solution of sodium thiosulfate (25 ml) (and twice with 5% aqueous solution of sodium hydrogencarbonate -25 ml- when the nucleophile was acetic or formic acid), dried over anhydrous Na_2SO_4 and evaporated in vacuo. Reaction products were purified by washing with hexane through a short column packed with silica.

12.- L. Brandsma: *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, New York, 1988, p. 143.

(Received in UK 22 March 1990)