

IODOFUNCTIONALIZATION OF ALKYNYSULFIDES WITH IPy_2BF_4

José Barluenga,* Pedro J. Campos, Fernando López, Isidro Llorente, and
Miguel A. Rodríguez

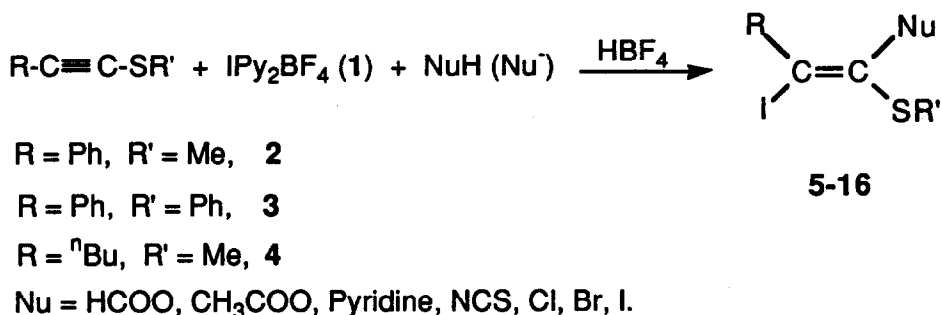
Departamento de Química Organometálica, Facultad de Química, Universidad de
Oviedo, 33071-Oviedo, Spain

Abstract: Alkynylsulfides react with bis(pyridine)iodine (I) tetrafluoroborate (1) and nucleophiles in a regio- and stereoselective electrophilic addition reaction to give 1-functionalized 2-iodovinylsulfides.

Vinylsulfides are important intermediates with substantial applications in organic synthesis.¹ They have been frequently used as umpoled synthons (acyl anion equivalents)² or enol substitutes.³ Its behaviour is as a masked carbonyl group due to its facility of hydrolysis with mercury (II) salts.⁴ These compounds can be synthesized by the following general methods; additions of electrophilic or nucleophilic reagents to alkynylsulfides,⁵ additions of sulfur containing compounds to alkynes,⁶ eliminations of thiols from bithioacetals,² olefinations via Wittig-like^{4,7} or Peterson^{2,8} processes, and other methods.² In most cases, non-functionalized vinylsulfides are formed and mixtures of regio and stereoisomers are often obtained.

We have recently described the iodofunctionalization of alkynes⁹ and 1-haloalkynes¹⁰ with bis(pyridine)iodine (I) tetrafluoroborate (1) and different nucleophiles. Now we want to report the preparation of α -functionalized β -iodovinylsulfides starting from alkynylsulfides and 1.

Thus, alkynylsulfides¹¹ react with 1 and the corresponding nucleophile in the presence of two equivalents of tetrafluoroboric acid, to avoid the competing addition of pyridine from reagent 1, to give, in a 'one-pot' procedure at room temperature, the 2-iodovinylsulfides functionalized in 1-position (see Table and Scheme 1).¹² When the acid treatment was omitted, pyridine itself worked as nucleophile yielding pyridinium salts 8 and 9.



Scheme 1

Only one regio and stereoisomer was observed in all the cases according to the ¹H-, ¹³C-nmr and MS spectra. Although the spectral data correlate fairly well with those expected for the reported compounds they alone can not be used to establish unequivocally the absolute configuration of the new vinylsulfides.

The determination of the regiochemistry of the reaction products was based on the identification of the olefinic carbons in the ¹³C-nmr spectra taking into account the large shielding induced by the iodine atom and on 2D heteronuclear correlation experiments¹³ carried out on compounds **8**, **12** and **13**. The observation of a long range coupling between the hydrogens of the methylthio group and the more deshielded olefinic carbon clearly establish the configuration of the vinyl sulfides (**5-16**) as shown in Scheme 1.

On the other hand, the assignments of the Z- configuration to the reported compounds was based on NOE-difference experiments.¹³ Again compounds **8**, **12**, and **13** were taken as a model. According to the proposed stereochemistry of the double bond, low power irradiation of the methyl groups in all three compounds only showed positive NOE for **8** due to the dipolar interaction of these protons with the *ortho* protons of the pyridine substituent. The absence of any NOE between the groups R and R' would be in agreement with their *trans* arrangements around the carbon-carbon double bond.

The obtained regioisomers was in concordance with the high stabilization of positive charge on carbon that bears the sulfur atom due to the resonance effect of electronic pairs. These regio and stereochemical results are in agreement with the previously postulated mechanism through a cyclic iodonium ion intermediate.^{9b}

Table. Synthesis of α -functionalized β -iodovinylsulfides

Alkyne	Nucleophile	Solvent	Time (h)	Product	Yield (%) ^a
2	HCOOH ^{b,c}	HCOOH/CH ₂ Cl ₂ (1:1)	14	5^d	72
2	AcOH ^c	AcOH/CH ₂ Cl ₂ (1:1)	14	6^d	68
4	AcOH ^c	AcOH/CH ₂ Cl ₂ (1:1)	14	7^d	83
2	Pyridine ^{c,e}	CH ₂ Cl ₂	1	8	70
3	Pyridine ^{c,e}	CH ₂ Cl ₂	1	9	41
2	KSCN ^f	MeCN/H ₂ O (5:1)	20	10	70
4	KSCN ^f	MeCN/H ₂ O (5:1)	20	11	91
2	LiCl ^f	MeCN/H ₂ O (5:1)	20	12	84
4	LiCl ^f	MeCN/H ₂ O (5:1)	20	13	76
2	LiBr ^f	MeCN/H ₂ O (5:1)	20	14	82
2	NaI ^f	MeCN/H ₂ O (5:1)	16	15	64
4	NaI ^f	MeCN/H ₂ O (5:1)	16	16	67

^aYield of isolated products, relative to starting **1** and not optimized. The resulting products were purified by column chromatography (silica, hexane or hexane-ether 98:2) to eliminate the unreacted starting alkynylsulfide. GC purity >95%. ^b85% aqueous solution. ^cAcid treatment was omitted. ^dThe product could not be purified because of decomposition. ^eFrom compound **1**. ^fMole ratio Nu:**1** = 3:1.

Acknowledgements. This research was supported by DGICYT (Project PB88-500).

References and notes.

- 1.- G. C. Barret, in *Comprehensive Organic Chemistry*, D. Barton, D. Ollis, Eds., Pergamon, Oxford, UK, 1979, vol. 3, cap. 11.4, p. 80.
- 2.- D. J. Ager, in *Unpoled Synthons*, T. A. Hase, Ed., Wiley, New York, 1987, cap. 2, p. 56.
- 3.- B. M. Trost, A. C. Lavoie, *J. Am. Chem. Soc.*, **1983**, *105*, 5075.
- 4.- E. J. Corey, J. I. Shulman, *J. Org. Chem.*, **1970**, *35*, 777.
- 5.- See ref. 1, p. 86.
- 6.- T. J. Barton, R. G. Zika, *J. Org. Chem.*, **1970**, *35*, 1729. M. G. Missakian, R. Ketcham, A. R. Martin, *J. Org. Chem.*, **1974**, *39*, 2010. G. H. Schmidt, in *The Chemistry of the Carbon-Carbon Triple Bond*, S. Patai, Ed., Wiley, New York, 1978, part 1, cap. 8, p. 306. P. B. D. de la Mare, R. Bolton, *Electrophilic Additions to Unsaturated Systems*, Elsevier, Amsterdam, 1982, cap. 9, p. 311.
- 7.- J. I. Grayson, S. Warren, *J. Chem. Soc., Perkin Trans. I*, **1977**, 2263.
- 8.- D. J. Ager, *J. Org. Chem.*, **1984**, *49*, 168.
- 9.- a) J. Barluenga, M. A. Rodríguez, J. M. González, P. J. Campos, G. Asensio, *Tetrahedron Lett.*, **1986**, *27*, 3303. b) J. Barluenga, M. A. Rodríguez, P. J. Campos, *J. Org. Chem.*, **1990**, *55*, 3104.
- 10.- J. Barluenga, M. A. Rodríguez, P. J. Campos, G. Asensio, *J. Am. Chem. Soc.*, **1988**, *110*, 5567. J. Barluenga, M. A. Rodríguez, P. J. Campos, *Tetrahedron Lett.*, **1990**, *31*, 2751.
- 11.- Prepared by reaction of lithium alkynides with dimethyl or diphenyl sulfides at -50°C in THF. See: L. Bradsmá, *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, Amsterdam, 1988.
- 12.- Typical procedures for iodofunctionalization of alkynylsulfides, see reactions of IPy_2BF_4 with alkynes⁹ and 1-haloalkynes.¹⁰
- 13.- All the experiments were carried out according to the standard Bruker-software.

(Received in UK 17 October 1990)