

iodo-CARBOFUNCTIONALIZATION OF ALKYNES WITH AROMATIC RINGS AND IPy_2BF_4

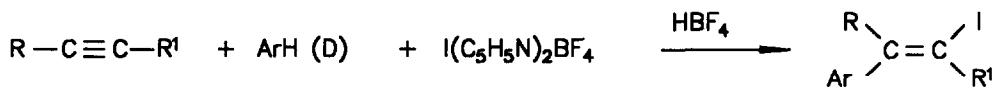
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Abstract: Alkynes react with bis(pyridine)iodine(I)tetrafluoroborate (**1**) and aromatic rings (activated, nonactivated and deactivated) in a Friedel-Crafts-type alkylation reaction to give, in a regio- and stereoselective way, *trans*- β -iodostyrene derivatives.

Electrophilic addition to alkynes have been used to promote carbon-carbon bond formation: alkyl halides in the presence of Lewis acid and other sources of carbenium ions,¹ hydrogen bromide to compounds containing two suitable situated triple bond,^{1a,2} acylium salts in the presence of aromatic compounds,³ and a mixture of iodine and copper(I) cyanide to (perfluoroalkyl)alkynes.⁴

We have described the iodo-carbofunctionalization of internal alkynes with bis(pyridine)iodine(I) tetrafluoroborate (**1**) and anisole.⁵ These processes represent synthetical examples of the application of alkynes as alkylating agents in Friedel-Crafts-type alkylation reactions. Only a few cases with alkynes have been previously described.^{3,6} The high importance of carbon-carbon bond formation in organic chemistry prompted us to study this reaction with different alkynes and aromatic rings (see Scheme 1 and Table).



R = Ph, *n*-Bu; R' = H, Me

ArH (D) = benzene, benzene-*d*₆, toluene, *p*-xylene, mesitylene,
pentamethylbenzene, bromobenzene, anisole, naphthalene

Scheme 1

The reaction is quite general and allows the functionalization of terminal and internal alkynes with activated, nonactivated and deactivated aromatic rings.⁷

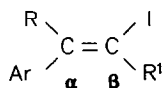
The reaction products were purified by column chromatography (silica, hexane-ether 98:2) to eliminate the small amounts of unreacted alkyne and aromatic compound (and the corresponding iodoarenes when the nucleophile was anisole or mesitylene). All the compounds show ¹H, ¹³C NMR spectroscopy and mass spectrometry according with the proposed structures. The stereochemistry was determined by NOE experiments and the regiochemistry was confirmed based on ¹³C chemical shift of carbon that bears the iodine atom.

Anti-addition products were only yielded, which is in agreement with the previously proposed mechanism through a vinyleneiodonium ion.⁸

On the other hand, the Friedel-Crafts-type alkylation reaction on the aromatic ring give, in some cases, different isomers in concordance with the electronic effect of their substituents: a mixture of *ortho*- and *para*-substitution with toluene (39:61) and bromobenzene (5:95), the *para*-isomer with anisole and a mixture of 1- and 2-isomer with naphthalene (84:16).

It is noteworthy the possibility to introduce different aromatic compounds as nucleophile, in special when the aromatic ring is deactivated like in bromobenzene.

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Table: Synthesis of *trans*- β -iodostyrene derivatives

R	R ¹	ArH (D)	Yield (%) ^a	¹³ C-NMR δ (ppm) ^b	
				C(α)	C(β)
Ph	H	Benzene	75	153.2	80.8
Ph	H	Benzene- <i>d</i> ₆	68	152.2	79.1
Ph	H	Toluene	92 ^c <i>ortho</i> (39)	152.2	79.0
			<i>para</i> (61)	152.3	78.0
Ph	H	<i>p</i> -Xylene	78	152.3	78.7
Ph	H	Mesitylene	75	150.5	79.0
Ph	H	Pentamethylbenzene	94	151.4	77.6
Ph	H	Bromobenzene	20 ^c <i>ortho</i> (5)	151.7	80.8
			<i>para</i> (95)	151.8	79.8
Ph	Me	Anisole	60 ^d	148.3	100.3
Ph	Me	Naphthalene	90 ^c 1-naphthyl (84)	145.5	100.2
			2-naphthyl (16)	145.6	100.3
<i>n</i> -Bu	H	Mesitylene	60	151.2	78.8

^aYield of isolated products, relative to starting **1** and not optimized.

^bSpectra were recorded on a Bruker AC-300 spectrometer in DCCl₃ using TMS as internal standard.

^cIsomers ratios, determined by ¹H NMR spectra of the crude reaction. Isomers could not be separated.

^dIsomer *para* was only obtained.

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- 7 Typical experimental procedure for iodofunctionalization of alkynes:
To a solution of **1** (5 mmol, 1.86 g) in anhydrous methylene dichloride (25 ml) cooled at -80°C , tetrafluoroboric acid (10 mmol, 1.40 ml of ethereal 54% solution) and the alkyne were added under inert atmosphere. After twenty minutes of stirring, the aromatic compound (5 mmol) dissolved in methylene dichloride (5 mmol) was introduced into the reaction flask. The solution was allowed to arise at -60°C during one hour and then hydrolyzed with water (50 ml), extracted with methylene dichloride (3 x 25 ml), washed with 5% aqueous solution of sodium thiosulfate (25 ml), dried over anhydrous sodium sulphate and evaporated in vacuo. Reaction products were purified by column chromatography (silica, hexane-ether 98:2).
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