sp-Carbon–Iodine Bond Cleavage of Alkynyl(phenyl)iodonium Salts, Novel Synthesis of (Alkylethynyl)triphenylphosphonium Salts

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Substitutions of (alkylethynyl)phenyliodonium tetrafluoroborates with triphenylphosphine in sunlight provide a useful method for the synthesis of (alkylethynyl)triphenylphosphonium tetrafluoroborates.

Highly electron deficient alkynylphosphonium salts act as good Michael acceptors for carbon, nitrogen, oxygen, and sulphur nucleophiles. The Michael addition provides a useful tool for the synthesis of substituted vinylphosphonium salts[1] and a variety of heterocyclic compounds.[2] The most direct and convenient route for the synthesis of alkynylphosphonium salts involves the substitution reaction of halogenoalkynes with phosphines.[3] The method is readily applicable to the reaction of arylhalogenoacetylenes but not alkylhalogenoacetylenes. Reaction of alkylhalogenoacetylenes with phosphines produces a mixture of products derived from nucleophilic attack at halogen, α- and β-carbon atoms, as well as from further conversion of the initial products.[4]

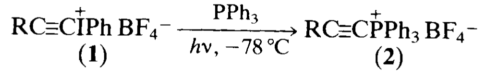
We have demonstrated that vinyliodonium tetrafluoroborates act as highly activated species of vinyl iodides in nucleophilic substitutions because of the high leaving ability of the hypervalent iodine(III) substituent.[5] Thus, alkynyliodonium tetrafluoroborates seem to be much more reactive and suitable species compared to halogenoalkynes in nucleophilic substitutions with phosphines. We report here an efficient method for the synthesis of (alkylethynyl)triphenylphosphonium salts (**2**).

The required alkynyliodonium tetrafluoroborates (**1**) were prepared from the corresponding alkynylsilanes in good yields by the method developed recently.[6] More conveniently, (**1**) can also be synthesized from the corresponding 1-alkynes. For

Table 1. Synthesis and selected spectral data of alkynylphosphonium salts (**2**).

Products[g]	^{13}C n.m.r. (δ)[a] α-C	^{13}C n.m.r. (δ)[a] β-C	I.r. (cm^{-1})[b]	F.a.b.-m.s. (*m/z*)[c]
(**2a**)	60.1(192)[d]	121.8(32)[e]	2210, 1055	301
(**2b**)	61.0(191)[d]	125.4(32)[e]	2200, 1055	399
(**2c**)	61.1(191)[d]	124.9(31)[e]	2200, 1055	369
(**2d**)	61.1(189)[d]	128.1(29)[e]	2190, 1055	369
(**2e**)[f]	60.1(186)[d]	131.1(29)[e]	2175, 1050	343

[a] In CDCl$_3$. [b] In CHCl$_3$. [c] Peaks corresponding to (M–BF$_4$)$^+$. [d] Coupling constants $^1J(^{13}\mathrm{C}–^{31}\mathrm{P})$ in Hz. [e] Coupling constants $^2J(^{13}\mathrm{C}–^{31}\mathrm{P})$ in Hz. [f] M.p. 178—181 °C. [g] Formed in quantitative yield.

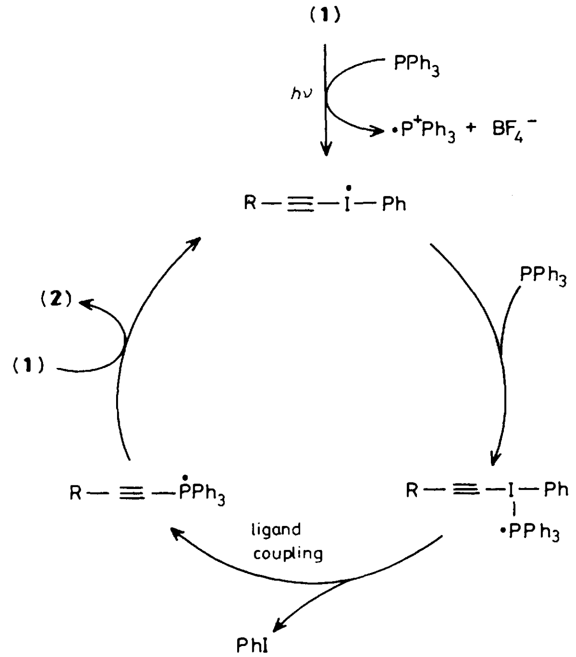


$$\underset{(1)}{\mathrm{RC{\equiv}C\overset{+}{I}Ph\,BF_4^-}} \xrightarrow[h\nu,\,-78\,^\circ\mathrm{C}]{\mathrm{PPh_3}} \underset{(2)}{\mathrm{RC{\equiv}C\overset{+}{P}Ph_3\,BF_4^-}}$$

a; R = Me
b; R = n-C$_8$H$_{17}$
c; R = cyclo-C$_5$H$_9$CH$_2$
d; R = cyclo-C$_6$H$_{11}$
e; R = Bu^t

Bu^{t}C≡CBF$_3^-$ Li$^+$
(**3**)

Scheme 1



Scheme 2

example, 3,3-dimethylbut-1-ynylborate (**3**), prepared from 3,3-dimethylbut-1-yne and n-butyl-lithium in the presence of boron trifluoride–diethyl ether *in situ*,[7] on treatment with boron trifluoride-activated iodosylbenzene (1.6 mol. equiv.) in dichloromethane at room temperature for 3 days followed by quenching with excess of aqueous sodium tetrafluoroborate, afforded an 85% yield of the alkynyliodonium tetrafluoroborate (**1e**).

Nucleophilic substitutions of halogenoalkynes with triphenylphosphine usually require 2—3 days at room temperature.[3,4] Using highly reactive (alkylethynyl)phenyliodonium tetrafluoroborates (**1**), the reaction with triphenylphosphine proceeds smoothly even at −78 °C; treatment of a solution of prop-1-ynyliodonium salt (**1a**) in tetrahydrofuran with triphenylphosphine (1.2 mol. equiv.) in sunlight at −78 °C for 2 h afforded prop-1-ynyltriphenylphosphonium tetrafluoroborate (**2a**) in quantitative yield. Similarly, phosphonium salts (**2b**—**e**) were prepared (Table 1).

^{13}C Chemical shifts and ^{13}C–^{31}P coupling constants of acetylenic carbons in (**2**) (Table 1) are in good agreement with those reported for prop-1-ynyltriphenylphosphonium bromide.[8] Fast atom bombardment mass spectra (f.a.b.-m.s.) showed relatively abundant fragments corresponding to the cationic portion of the salts (**2**). I.r. spectra of (**2**) showed sharp bands at 2200 cm^{-1} and broad bands at 1050 cm^{-1} characteristic of the triple bond and BF$_4^-$ anion, respectively.

The mechanism of this substitution of alkynyliodonium salts (**1**) with triphenylphosphine is not yet clear, but we propose a reaction pathway involving radicals on the basis of the observation that the substitution requires sunlight and does not proceed in the dark (Scheme 2). Thus, the reaction of (**1b**) with triphenylphosphine at −78 °C for 2 h in the dark did not give the salt (**2b**) at all and a large amount of (**1b**) and triphenylphosphine were recovered unchanged. Furthermore, Ptitsyna and his co-workers have reported that the reaction of diphenyliodonium salts with triphenylphosphine proceeds by a radical chain mechanism.[9]

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