Reaction of (Perfluoroalkyl)alkynes with Iodine and some of its Derivatives

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Iodine and some of is derivatives, such as ICl, ICN, and IF, react, under relatively mild conditions, with (perfluoroalkyl)alkynes R_F–C≡C–H to afford regiospecifically the corresponding 1-iodo perfluorinated alkenes.

In contrast to trifluoropropyne CF_3–C≡C–H, the chemistry of which was fully investigated in the 1950's,[1] only a few examples of the reactions of long-chain (perfluoroalkyl)-alkynyl analogues have been described,[2] owing mainly to their relative inaccessibility. In the course of our studies on aliphatic perfluorinated compounds, we recently reported new convenient and efficient preparations of various long-chain (perfluoroalkyl)alkynes.[3,4] The synthesis of the terminal (perfluoroalkyl)acetylenes R_F–C≡C–H (R_F = C_4F_9, C_6F_{13}, C_8F_{17}), by means of a simple electrochemical technique, was a considerable improvement over the previously reported multistep chemical processes.[5]

In this communication, we report results concerning the addition reactions of iodine and some of its derivatives (IF, ICl, ICN) to these acetylenes, which afford, regiospecifically, substituted fluorinated olefins in high yields.

$$\underset{(1)}{R_F\text{–C}{\equiv}\text{C–H}} + \text{I–Y} \rightarrow \underset{(2)}{R_F\text{–C(Y)C}{=}\text{C(I)H}}$$

a; Y = I
b; Y = Cl
c; Y = CN
R_F = C_4F_9, C_6F_{13}, C_8F_{17}

Table 1.

Y	Method[a]	Solvent	Temp. (°C)	Time (h)	Product[b]	Isolated yield (%)
I	A	MeCN	85	8	**(2a)**	75
I	A	MeCN	65	24	**(2a)**	87
I	A	AcOH	120	12	**(2a)**	85
I	A	$CHCl_3$	65	24	none	—
Cl	B	AcOH	55	3	**(2b)**	75
Cl	C	MeCN	90	6	**(2b)**	60
Cl	C	MeCN	90	18	**(2b)**	72
CN	D	MeCN	90	6	**(2c)**	65
CN	D	MeCN	90	18	**(2c)**	85
F	E	MeCN	65	8	**(2a)** + **(3)**	**(2a)** 25 **(3)** 55

[a] A: Alkyne **(1)** (10 mmol) added to powdered I_2 (15 mmol) in 10 ml solvent; B: alkyne **(1)** (10 mmol) added to a 5 M solution of commercial ICl in AcOH (10 ml); C: alkyne **(1)** (10 mmol) added to $CuCl_2$ and I_2 (50 mmol; ratio $CuCl_2 : I_2 = 1$) in 100 ml MeCN; D: alkyne **(1)** (10 mmol) added to CuCN and I_2 (50 mmol; ratio CuCN: $I_2 = 1$) in 100 ml MeCN; E: alkyne **(1)** (10 mmol) added to KF and I_2 (15 mmol; ratio KF : $I_2 = 1$) in 10 ml MeCN.[b] Fully characterized by ^1H and ^{19}F n.m.r., i.r., and mass spectra. [^1H N.m.r. (CCl_4, Me_4Si) δ **(2a)** 8.27, **(2b)** 7.38, **(2c)** 6.90. ^{19}F N.m.r. (CCl_4, internal C_6F_6) $\delta_{CF_{2\alpha}}$ **(2a)** 98.7, **(2b)** 99.3, **(2c)** 102.3, **(3)** 97.6 p.p.m.]

Iodination was usually carried out by heating the acetylene with an excess of iodine in a suitable solvent. In the chloroiodination reactions, iodine monochloride was either pre-formed, or else it was generated *in situ* from an equimolecular mixture of copper(II) chloride and iodine.[6] Cyanogen iodide ICN may be formed from the action of iodine on mercury(II) cyanide,[7] but, in our case, this method led to acetylenic mercury(II) by-products. However, the reaction of the (perfluoroalkyl)alkynes with an equimolar mixture of copper(I) cyanide and iodine proceeded smoothly in acetonitrile to give the corresponding 1-iodo-2-cyano-olefins.

The reaction of potassium fluoride on iodine, which is known to be a good source of iodine monofluoride in the preparation of fluoroalkyliodides from perfluoro-olefins,[8] was used; unfortunately, in this case, the corresponding fluoroiodoalkene was not obtained; only a mixture of the di-iodo-olefin and the 1-iodo-2-perfluoroalkylacetylene was produced (equation 1).†

$$\underset{\mathbf{(1)}}{R_F\text{–}C\equiv C\text{–}H} \longrightarrow \underset{\mathbf{(2a)}\,(25\%)}{R_FC(I)\text{=}C(I)H} + \underset{\mathbf{(3)}\,(55\%)}{R_F\text{–}C\equiv C\text{–}I} \quad (1)$$

Table 1 shows the experimental conditions used and the results obtained in the case of the (perfluorohexyl) acetylene.

The regiospecificity of the addition reaction was clearly shown by the easy base-catalysed elimination reaction, which affords only the 1-iodo-2-perfluoroalkylacetylene in a quantitative yield (equation 2). Note that in the case of ICl and ICN additions, no traces of $R_F\text{–}C\equiv C\text{–}Cl$ or $R_F\text{–}C\equiv C\text{–}CN$, which would come from the dehydroiodination of the opposite addition reaction products $R_F\text{–}C(I)\text{=}C(Y)H$ (Y = Cl, CN), were detected.

$$R_F\text{–}C(Y)\text{=}C(I)H \xrightarrow[\text{room temp., 0.5 h}]{\text{KOH, MeOH}} R_F\text{–}C\equiv C\text{–}I \quad (2)$$

Such a result confirms others, particularly the hydration of the alkynes $R_F\text{–}C\equiv C\text{–}H$ leading to the ketone $R_F\text{–}CO\text{–}Me$,[9] concerning the polarity of the triple bond, which is that usually found in hydrocarbon alkynes.

It can then be concluded, from these results, that trifluoropropyne $CF_3\text{–}C\equiv C\text{–}H$, the polarity of which was suggested to be the opposite,[1] is a special case, due to the unusual electronic effects of the trifluoromethyl group.

On another hand, all reactions produced only one isomer, which is assumed to be the (*Z*)-isomer (referring to the ease of the elimination reaction, n.m.r. spectra, and to other results in the same area[10]). This (*Z*)-isomer would come from a *cis*-addition on the triple bond, assuming the elimination to be *trans*.

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† It is assumed that the 'IF' addition product is unstable and leads to the acetylenic iodide by an easy HF elimination under the experimental conditions:

$$R_F\text{–}C\equiv C\text{–}H \xrightarrow{+IF} [R_F\text{–}CF\text{=}CIH] \xrightarrow{-HF} R_F\text{–}C\equiv C\text{–}I$$

If KF is added after 2—3 h reaction, only the di-iodo-olefin **(2a)** is produced.

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