An Efficient Electrochemical Route to (Perfluoroalkyl)alkynes

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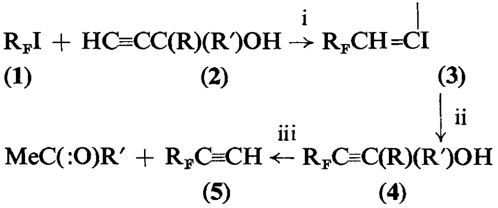
Electrocatalytic addition of perfluoroalkyl iodides to 3-hydroxy-3-alkylbut-1-ynes, followed by dehydroiodination and thermal cleavage in basic medium, leads to an easy and efficient preparation of (perfluoroalkyl)alkynes.

Perfluorinated alkynes are potential intermediates for the introduction of perfluoroalkyl chains in organic compounds and have previously been prepared from the corresponding perfluoroalkyl iodides. The lower alkynes $R_F{-}C{\equiv}C{-}H$ ($R_F = CF_3, C_2F_5$, or i-C_3F_7) were the first reported,[1,2] and their chemistry was later developed.[3] Long-chain homologues have been prepared more recently either from bromination, dehydrobromination, and debromination reactions,[4] or from copper-initiated couplings between perfluoroalkyl iodides and unsaturated substrates.[5,6] However, these processes often involve multistep routes which lead only to low to moderate yields.

In our laboratory, we have developed the electrochemical reduction of perfluoroalkyl iodides on mercury[7] and the electrolytic additions of these iodides to various alkenes. We recently found that a technique, which involves electrolysis at a carbon fibre cathode of the organic phase dispersed in a water–KCl electrolyte, led to a considerable improvement,[8] and we now report the first use of this electrochemical method in a convenient and quantitative synthesis of long-chain (perfluoroalkyl)acetylenes, $R_F{-}C{\equiv}C{-}H$.



$$\begin{tikzcd} \underset{(1)}{R_FI} + \underset{(2)}{HC{\equiv}CC(R)(R')OH} \arrow[r, "i"] & \underset{(3)}{R_FCH{=}CI{-}C(R)(R')OH} \arrow[d, "ii"] \\ MeC(:O)R' + \underset{(5)}{R_FC{\equiv}CH} & \underset{(4)}{R_FC{\equiv}C(R)(R')OH} \arrow[l, "iii"'] \end{tikzcd}$$

a; R = R′ = H
b; R = Me, R′ = H
c; R = R′ = Me
d; R = Me, R′ = Et

Scheme 1. i, Carbon fibre cathode; ii, KOH, MeOH, 2 h, room temp.; iii, NaOH, heat.

Perfluoroalkyl iodides R_FI (**1**; $R_F = C_4F_9, C_6F_{13}$) react with alkynes (**2a**—**d**), according to step (i), Scheme 1, in an electrolytic cell where the cathodic compartment consisted of carbon fibres, in water as solvent, and with KCl as the electrolyte.† The products (**3**) of this reaction were isolated by decantation and extraction of the organic phase, and purified by vacuum distillation. A mixture of *cis*- and *trans*-isomers was obtained in the case of compounds (**3a**) and (**3b**), but only the pure *trans*-(**3c**) and *trans*-(**3d**) were isolated. The identification of the intermediates, and the mechanism and stereochemistry of the reaction will be described elsewhere.

If the electrolysis is continued after the formation of (**3**), the increase of pH in the cathodic compartment, which results from the electrolysis of the aqueous phase, may lead to the formation of the perfluorinated alkyne (**4**) directly in the cell. However, this compound is more easily and quantitatively (95%) obtained by a dehydroiodination of *trans*-(**3**), step (ii), Scheme 1. Thermal cleavage of the alkynes (**4**) on sodium hydroxide pellets leads then to the required (perfluoroalkyl)alkynes (**5**), step (iii), Scheme 1. This is a new example of cleavage by alkali-metal alkoxides of highly branched tertiary alcohols,[9] and data are shown in Table 1.

Table 1. Cleavage reactions of alkynes (**4**).

R_F	R′	Temperature range[a] (°C)	B.p (°C) of (**5**)	% yield[b] of (**5**)
C_4F_9	Me	60—120	42	90
C_4F_9	Et	80—120	42	85
C_6F_{13}	Me	95—160	94—96	90
C_6F_{13}	Et	95—160	94—96	80

[a] The first temperature corresponds to the beginning of the cleavage reaction; the second one corresponds to the end of distillation.
[b] Yields are given from the amount of (**4**) which has effectively reacted. When higher temperatures are used, some tars are obtained.

It seems reasonable to assume that the electrochemical addition [step (i)] involves a catalytic process initiated at the cathode; this is in agreement with mechanisms proposed in previously described chemical additions of R_FI to unsaturated systems.[10]

The present results show that (perfluoroalkyl)alkynes may be obtained from perfluoroalkyl iodides in good yields (80—90% based on consumed R_FI), by means of a simple electrochemical technique, in which no organic solvent and no polluting agents are used.

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† In a typical experiment 0.22 mol (50 ml) of $C_6F_{13}I$ and 0.22 mol (25 ml) of (**2c**) were subjected to a current of 0.7 A for 2 h at room temperature. The cell consisted of a cathodic compartment containing 0.6 m^2 of carbon fibre (60 cm AGTF, 10000 fibres) and a carbon rod as anode; H_2O was the solvent and sat. KCl the electrolyte. The product (**3c**) was obtained in 98% yield (70%, based on $C_6F_{13}I$ consumed) and the current yield was 0.3 F mol^{-1} based on a total reduction of R_FI with 1 electron per molecule.

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