

Convenient Preparation of Unsymmetrical 1,2-bis(Perfluoroalkyl)ethynes

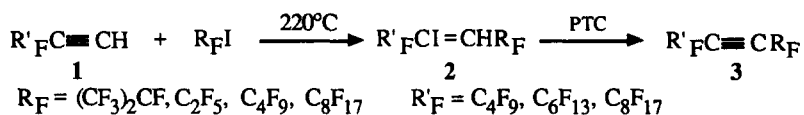
Véronique Sanchez and Jacques Greiner

Unité de Chimie Moléculaire, associée au CNRS, Université de Nice-Sophia Antipolis, Parc Valrose,
06108 Nice Cedex 02, France.

Abstract: An improved preparation of unsymmetrical perfluoroalkynes **3** is described using dehydroiodination of 1,2-bis(*F*-alkyl)iodoethenes **2** under phase transfer catalysis.

Perfluorooctyl bromide, a fluorocarbon used in *in vivo* oxygen-delivery systems,¹ is also radiopaque owing to the presence of its bromine atom, and investigated as a contrast agent in diagnosis.² In the course of developing new perfluorocarbons with improved radiopacity, we needed a convenient procedure for the preparation of perfluoroalkynes. These constitute versatile intermediates for the synthesis of fluorocarbons with several bromine or iodine atoms. Easy accesses to terminal perfluoroalkynes are available.³⁻⁵ Though 2-hexafluorobutyne has been known for a long time^{3,6a,7} and is commercially available, the synthesis of homologous long-chain perfluoroalkynes with an internal triple bond received little attention.^{3,8-10} The development of a convenient route allowing to introduce in one step, two different perfluoroalkyl chains in organic molecules under standard laboratory conditions was desirable.

The two main strategies used to prepare 1,2-bis-(perfluoroalkyl)acetylenes involve halogen or hydrogen halide elimination from an appropriate olefin.³ The first method requires the prior preparation of dihaloolefins ($R_F CX=CHR'_F$), either from 1,1,1-trihalopolyfluoroalkanes^{10,11} (which allowed the synthesis of symmetrical alkynes with poor yields, especially for higher molecular weight homologs^{6,10}) or from perfluoroalkylethenes⁷ by a time-consuming 6-step sequence. The second approach,⁷⁻⁹ the one we chose to improve, has been effected on a few examples by heating 1,2-bis(*F*-alkyl)haloethenes over potassium hydroxide pellets and distilling **3** off. Except for *F*-butyne,⁷ (Cf. scheme) the yields were very poor^{8,9} owing to the overheating of the process and the ease of polymerization of such compounds.



Since it had been noted that **2**, when treated with an aqueous or ethanolic alkaline media, undergoes substitution rather than elimination,¹² phase transfer catalysis (PTC) was tried.¹³ Compound **2** was obtained in 80-90% yield (*Z/E*= 95/5) by thermal addition¹⁴ (220°C) of perfluoroalkyl iodide on **1**.⁵ Dehydroiodination of **2**, in ether in the presence of a 30% aqueous solution of NaOH and tetrabutylammonium hydrogen sulphate as a phase transfer agent, led to the desired alkynes **3** in 50-65% yields (after distillation, based on consumed **2**). It can be noted that this selective (only **3** was detected by GLC) and effective elimination reaction (only the *Z* isomer reacted) was fast, especially for compounds with linear perfluoroalkyl chains. **2** ($R_F, R'_F = C_4F_9, C_2F_5, C_8F_{17}; C_6F_{13}, C_4F_9$) gave the corresponding alkynes **3** in about 1 h. The

elimination rate was considerably decreased with the perfluoroisopropyl chain. Thus, for **2** ($R_F = iC_3F_7$, $R'_F = C_6F_{13}$), the reaction required 5 h for completion and two further additions of PTC (2.5% eq) after one and two hours of stirring.

Because of these differences of reactivity (and the quantities on which we worked) it is essential, in order to obtain good yields and reproducibility, to stop the reaction when 70-80% of **2** (**Z**) is consumed and to proceed with work-up and distillation immediately thereafter. If these precautions are followed to avoid further degradation and polymerization, this process allows a fast and easy laboratory access to unsymmetrical **3**.

General procedure: An ether solution (50 mL) of **2** ($R_F = C_6F_{13}$, $R'_F = C_4F_9$) (25 g), 0.61 g (5% eq) of tetrabutylammonium hydrogen sulphate and an aqueous solution of NaOH (13.3 g in 40 mL) are stirred at room temperature for 75 min. After the usual work-up, the crude product is filtered over silica gel, then distilled, affording 10.1 g (68%, based on consumed **2**) of the alkyne **3**¹⁵ and 6.8 g of recyclable **2**.

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References and notes

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 - All new compounds were fully characterized by IR, ¹⁹F and ¹³C NMR, and elemental analysis; for example **3** ($R_F = C_6F_{13}$, $R'_F = C_4F_9$) bp: 56°C/15 mm Hg; IR (KBr): 2290 ($\nu_{C=C}$), 1240-1150 (ν_{C-F}); ¹⁹F NMR (CDCl₃, CFCl₃ reference): -84.6 (t, $J_{FF} = 10.3$ Hz, CF₃), -83.6 (t, $J_{FF} = 10.6$ Hz, CF₃), -104.2 and -104.6 (4F, CF₂C=CCE₂), -122.9, -124.2, -124.4 and -125.2 (8F, CF₂), -127.4 and -128.1 (4F, CF₃CE₂); ¹³C NMR (CDCl₃): 76.02 (C₁, tt, $^2J_{CF} = 38.4$ Hz, $^3J_{CF} = 5.9$ Hz), 76.14 (C₂, tt, $^2J_{CF} = 38.4$ Hz, $^3J_{CF} = 5.9$ Hz).
- 3** R_F, R'_F : C₄F₉, C₄F₉ 45%, 95°C/760 mm Hg; C₂F₅, C₈F₁₇ 46%, 55°C/15 mm Hg; iC₃F₇, C₆F₁₃ 59%, 43°C/15 mm Hg.