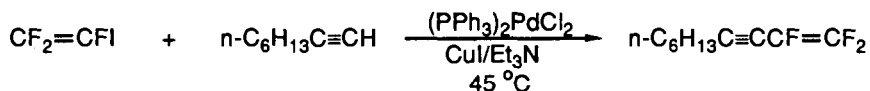


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FLUORINE CHEMISTRY SYNTHESIS

PREPARATION OF 1,1,2-TRIFLUORO-1-DECEN-3-YNE[†]

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A 100 mL two-necked flask equipped with a Teflon coated magnetic stirbar, a rubber septum and a reflux condenser connected to a source of nitrogen and mineral oil bubbler was charged with 0.63 g (0.9 mmol) of bis(triphenylphosphine)palladium dichloride¹, 0.19 g (1 mmol) of cuprous iodide² and 50 mL of triethylamine³. To the mixture 3.74 g (34 mmol) of 1-octyne³ was added *via* syringe and the dark solution was stirred at room temperature for 5 minutes, then 6.24 g (30 mmol) of trifluorovinyl iodide⁴ was added *via* syringe, and the reaction mixture was stirred⁵ at 45°C (oil bath

[†] The title compound has previously been prepared in 62% yield *via* palladium-catalyzed coupling reaction of the trifluorovinyl iodide with n-octynylzinc chloride [1]. We reported direct coupling reaction of fluorinated alkenyl iodides with terminal alkynes catalyzed by palladium/cuprous iodide [2].

temperature) for 4.5 hours⁶. The reaction mixture was cooled and poured into a 400 mL beaker containing 50 mL of ether. The flask was washed with ether (2×50 mL) and the solids were removed by filtration. The solids were transferred into a 400 mL beaker and washed with ether (3×50mL). The combined ether fractions were distilled (oil bath 60°C)⁷ to remove most of the ether, and then remaining ether and triethylamine were distilled under aspirator pressure at 65°C. The residue (5.2 g) was transferred to a 50 mL flask and distilled through a short path distillation apparatus under reduced pressure⁸ to give 3.7 g (64%) of 1,1,2-trifluoro-1-decen-3-yne, b.p. 54-55°C/5.8 mmHg, 100% pure by GLPC analysis. ¹⁹F NMR (CDCl₃, CFCl₃): -93.0 ppm (dd, J = 51.3 Hz, J = 26.9 Hz, 1F), -114.0 (dd, J = 114.8 Hz, J = 51.3 Hz, 1F), -171.2 (ddt, J = 114.8 Hz, J = 26.9 Hz, J = 4.9 Hz, 1F); ¹H NMR(CDCl₃, TMS): 2.47 ppm (m, 2H), 1.58 (pent, J = 7.2 Hz, 2H), 1.43(m, 2H), 1.31 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ¹³C NMR(CDCl₃, TMS): 159.04 ppm (ddd, J = 293.0 Hz, J = 282.2 Hz, J = 53.5 Hz), 116.94 (ddd, J = 220.1 Hz, J = 53.6 Hz, J = 30.4 Hz), 106.15 (m), 66.01 (ddd, J = 31.8 Hz, J = 8.7 Hz, J = 2.7 Hz), 32.23, 29.40, 28.87, 23.40, 20.10, 14.31; IR(CCl₄): 2930 (s), 2220 (s), 1755 (s), 1285 (s), 1130 (s): GC/MS: 190 (M⁺, 2.0), 141 (3.4), 119 (7.7), 99 (2.4), 69 (25.0), 43 (100).

NOTES

- 1 (PPh₃)₂PdCl₂ is available from Aldrich or can be readily prepared by reaction of PdCl₂ (Aldrich) with PPh₃ in DMF at room temperature [3].
- 2 Cuprous iodide (Aldrich) was washed with boiling THF and then dried under vacuum.
- 3 Triethylamine and 1-octyne were obtained from Aldrich, and used without purification.
- 4 Trifluorovinyl iodide was prepared by reaction of trifluorovinyl bromide with acid-washed zinc in DMF, with subsequent quenching of this zinc reagent with iodine[4].

- 5 We have found *slow* stirring to be desirable, as stirring at a high rate splashes the heterogeneous solution to the top of the flask and the catalysts then stick to the flask wall, necessitating longer reaction times.
- 6 Solids were precipitated and no remaining trifluorovinyl iodide was observed by ^{19}F NMR analysis of the reaction mixture solution.
- 7 Alternatively, triethylamine may be removed *via* a rotatory evaporator.
- 8 In order to avoid dimerization of the enyne [1], the temperature of the oil bath was maintained between 60°C and 110°C.

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