*Journal of Fluorine Chemistry, 52* (1991) 443–445

Received: April 3, 1991; accepted: April 24, 1991

FLUORINE CHEMISTRY SYNTHESIS

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

$$CF_2{=}CFI \quad + \quad n\text{-}C_6H_{13}C{\equiv}CH \xrightarrow[\text{CuI/Et}_3\text{N} \; 45\,^{\circ}\text{C}]{(PPh_3)_2PdCl_2} n\text{-}C_6H_{13}C{\equiv}CCF{=}CF_2$$

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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 dichloride[1], 0.19 g (1 mmol) of cuprous iodide[2] and 50 mL of triethylamine[3]. To the mixture 3.74 g (34 mmol) of 1-octyne[3] was added *via* syringe and the dark solution was stirred at room temperature for 5 minutes, then 6.24 g (30 mmol) of trifluorovinyl iodide[4] was added *via* syringe, and the reaction mixture was stirred[5] at 45°C (oil bath

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[†] 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].

0022-1139/91/$3.50

temperature) for 4.5 hours[6]. 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 pressure[8] 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. $^{19}F$ NMR ($CDCl_3$, $CFCl_3$): -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($CDCl_3$, 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); $^{13}C$ NMR($CDCl_3$, 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($CCl_4$): 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 $(PPh_3)_2PdCl_2$ is available from Aldrich or can be readily prepared by reaction of $PdCl_2$ (Aldrich) with $PPh_3$ 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.

## ACKNOWLEDGEMENT

We thank the National Science Foundation, the Air Force Office of Scientific Research and a Graduate Fellowship (PM) for support of this research.

## REFERENCES

1 F. Tellier, R. Sauvetre and J. F. Normant, J. Organometall. Chem., 328 (1987) 1.
2 Z. Y. Yang, and D. J. Burton, Tetrahedron Lett., 31 (1990) 1369.
3 R. F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, 1985, p.18.
4 P. L. Heinze and D. J. Burton, J. Org. Chem., 53 (1988) 2714.