Tetrahedron Letters,Vol.28,No.47,pp 5857-5860,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

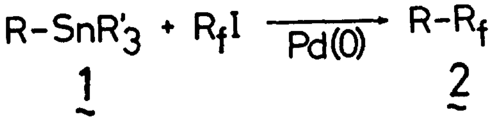
A FACILE PREPARATION OF 1-PERFLUOROALKYLALKENES AND ALKYNES. PALLADIUM CATALYZED REACTION OF PERFLUOROALKYL IODIDES WITH ORGANOTIN COMPOUNDS

Seijiro MATSUBARA*, Makoto MITANI, and Kiitiro UTIMOTO

Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Sakyo, Kyoto, 606 Japan

Summary: Alkenyl, allyl, and alkynylstannanes react with perfluoroalkyl iodides in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give alkenes and alkynes bearing perfluoroalkyl group.

Several perfluoroalkylation have been reported and utilized for the synthesis of various organofluorine compounds,[1] for example, the coupling reaction using perfluoroalkylcopper reagents[2] or perfluoroalkylzinc reagents,[3] the nucleophilic reaction to (perfluoroalkyl)phenyliodonium trifluoromethanesulfonate (FITS) reagent,[4] and the addition of perfluoroalkyl iodides to carbon-carbon multiple bond.[5,6,7] Although various types of perfluoroalkylation have been disclosed, direct coupling of an alkenyl group with a perfuoroalkyl halide giving perfluoroalkylated olefins has not been established. This paper describes a novel introduction of perfluoroalkyl group on olefinic or acetylenic carbon by the Pd(0) catalyzed cross-coupling reaction between organotin compounds and perfluoroalkyl iodides.[8]

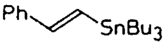
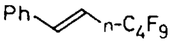
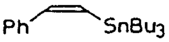
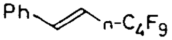
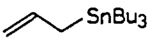
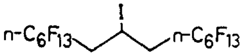
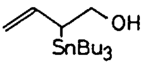
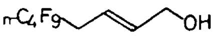
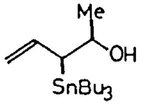
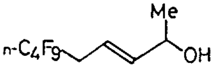


$$\underset{\mathbf{1}}{R\text{-}SnR'_3} + R_fI \xrightarrow{Pd(0)} \underset{\mathbf{2}}{R\text{-}R_f}$$

R: Alkenyl, Allyl, Alkynyl
R': Me, Bu
R_f: $n\text{-}C_4F_9$, $n\text{-}C_6F_{13}$, CF_3

A solution of $n\text{-}C_4F_9I$ (2.0 mmol, 0.70 g) in hexane (2.0 ml) was added dropwise to a mixture of (**E**)-1-phenyl-2-tributylstannylethene (1.0 mmol, 0.40 g) and $Pd(PPh_3)_4$ (0.10 mmol, 0.11 g) in hexane (3.0 ml).[9] The whole was stirred for 4 h at 70°C. The resulting mixture was poured into a mixture of ether and saturated KF aqueous solution (10 ml),[10] and extracted with ether. The separated organic layer was dried (Na_2SO_4) and concentrated. Purification by preparative thin layer chromatography (hexane) on silica gel gave (**E**)-1-phenyl-2-nonafluorobutylethene in 70% yield (0.23 g).

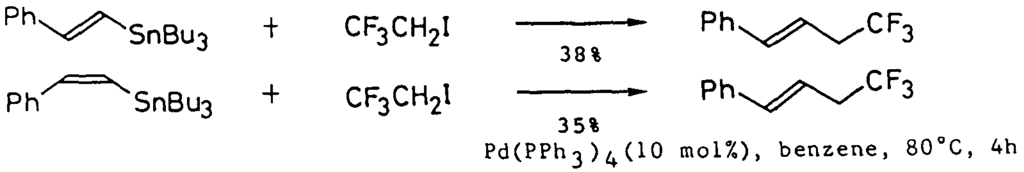
Alkenyl-, allyl-, and alkynylstannanes react analogously and results are summarized in Table. To examine stereospecificity of the reaction, Table. Introduction of Perfluoroalkyl Group into Organic Molecules[a]

Run	Substrates	R_fI (eq)	Temp	hr	Products	Yields(%)[b]
1		n-C_4F_9I(2.0)	70°C	4h		70%
2		CF_3I(excess)	80°C[c,d]	3h		11%[e]
3		n-C_4F_9I(2.0)	70°C	4h		70%
4		n-$C_6F_{13}I$(1.2)	R.T.	1h		100%[e]
5		n-$C_6F_{13}I$(3.0)	70°C	3h		64%
6		CF_3I(excess)	R.T.[c,d]	3h		24%[e]
7	 [f]	n-C_4F_9I(2.0)	70°C	4h		52%
8	 [f]	n-C_4F_9I(2.0)	70°C	4h		68%
9	$Me_3SnC{\equiv}C(CH_2)_5Me$	n-$C_6F_{13}I$(2.0)	70°C	6h	n-$C_6F_{13}C{\equiv}C(CH_2)_5Me$	55%[e]
10	$Me_3SnC{\equiv}C(CH_2)_4OTHP$	n-C_4F_9I(2.0)	70°C	6h	n-$C_4F_9C{\equiv}C(CH_2)_4OTHP$	60%
11	$Me_3SnC{\equiv}CPh$	n-$C_6F_{13}I$(2.0)	70°C	6h	n-$C_6F_{13}C{\equiv}CPh$	27%[e]

a) One mmol of substrate, 1.2-3.0 mmol of iodide, 0.1 mmol of $Pd(PPh_3)_4$, and 5 mL of hexane were employed. b) Isolated yields unless otherwise noted. c) Benzene was used as solvent. d) Bath temperature. Excess CF_3I was refluxing during reaction. e) ^{19}F-NMR yield using CF_3CO_2Et as an internal standard. f) See reference 11.

(E)-1-phenyl-2-tributylstannylethene and (Z)-1-phenyl-2-tributylstannylethene were treated with n-C_4F_9I under the same condition. The products were only (E)-1-phenyl-2-nonafluorobutylethene in both cases (run 1, 4). 2-Tributylstannyl-3-buten-1-ol and 3-tributylstannyl-4-penten-2-ol can be converted to perfluoroalkyl substituted compounds (run 9, 10) irrespective of hydroxyl group.

The above method can be applied to 1-iodo-2,2,2-trifluoroethane and **E**-alkene was obtained stereoselectively.



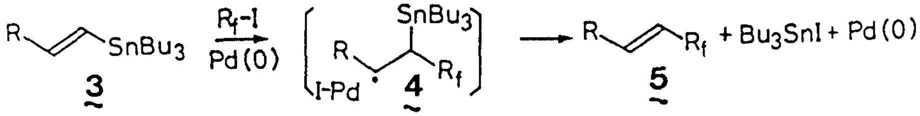
Acknowledgement: Financial support by Research Aid of Inoue Foundation of Science is acknowledged.

References and Notes

1. M.R.C. Gerstenberger and A. Haas, *Angew. Chem. Int. Ed. Engl.*, 20, 647(1981); T. Fuchikami, *J. Syn. Org. Chem. Jpn.*, **42**, 775(1984); P. Tarrant, *J. Fluorine Chem.*, 25, 69(1984); M. Schlosser, *Tetrahedron*, 34, 3(1978).
2. Y. Kobayashi and I. Kumadaki, *Tetrahedron Lett.*, **1969**, 4095; Y. Kobayashi, K. Yamamoto, and I. Kumadaki, *Tetrahedron Lett.*, **1979**, 4071; N.V. Kondratenko, E.P. Vechirko, and L.M. Yagupolskii, *Synthesis*, **1980**, 932; K. Matsui, E. Tobita, M. Ando, and K. Kondo, *Chem. Lett.*, **1981**, 1719; H. Suzuki, Y. Yoshida, and A. Osuka, *Chem. Lett.*, **1982**, 135; D.M. Wiemers and D.J. Burton, *J. Am. Chem. Soc.*, **108**, 832(1986).
3. N. Ishikawa and T. Kitazume, *J. Syn. Org. Chem. Jpn.*, **41**, 432(1983); T. Kitazume and N. Ishikawa, *Chem. Lett.*, **1982**, 137 and 1453; T. Kitazume, N. Ishikawa, *J. Am. Chem. Soc.*, **107**, 5186(1985).
4. T. Umemoto, *J. Syn. Org. Chem. Jpn.*, 41, 251(1983); T. Umemoto, Y. Kuriu, and S. Nakayama, *Tetrahedron Lett.*, 23, 4101(1982); T. Umemoto and Y. Gotoh, *Bull. Chem. Soc. Jpn.*, 59, 439(1986).
5. The addition reaction has been effected by various manners. (a) Photolysis: R.N. Haszeldine and B.R. Steele, *J. Chem. Soc.*, **1953**, 1199. (b) Pyrolysis: K. Leedham and R. N. Haszeldine, *J. Chem. Soc.*, **1954**, 1634. (c) Electorolysis: P. Calas, P. Moreau, and A. Commeyras, *J. Chem. Soc. Chem. Commun.*, **1982**, 433. (d) AIBN: N. O. Brace and J. E. Van Elswyk, *J. Org. Chem.*, **41**, 766 (1976). References cited therein.
6. D.J. Burton and L.J. Kehoe, *J. Org. Chem.*, **36**, 2596(1971); P.L. Coe and

N.E. Milner, *J. Organomet. Chem.*, **39**, 395(1972); T. Fuchikami and I. Ojima, *Tetrahedron Lett.*, 25, 303 and 307(1984); Q.-Y. Chen and Z.-Y. Yang, *J. Fluorine Chem.*, 28, 2596(1985); *idem*, *J. Chem. Soc., Chem. Commun.*, **1986**, 498.

7. T. Ishihara, M. Kuroboshi, and Y. Okada, *Chem. Lett.*, **1986**, 1895; H. Urata, and H. Yugari, T. Fuchikami, *Chem. Lett.*, **1987**, 833.
8. The palladium catalyzed coupling reaction of organotin compounds with allyl halide, vinyl iodide, or acyl chloride, see; M. Kosugi, Y. Shimizu, and T. Migita, *Chem. Lett.*, **1977**, 1423; J. W. Labadie and J. K. Stille, *J. Am. Chem. Soc.*, 105, 6129(1983); F.K. Sheffy and J.K. Stille, *ibid.*, 105, 7173 (1983); W.F. Goure, M.E. Wright, P.D. Davis, S.S. Labadie, and J.K. Stille, *ibid.*, **106**, 6417 (1984).
9. Benzene can also be used as solvent and suitable for the reaction using CF_3CH_2I and CF_3I.
10. To remove organotin residue, aqueous KF solution is effective: J.E. Leibner and J. Jacobus, *J. Org. Chem.*, **44**, 449(1979).
11. Vinylmagnesium bromide (1.5 M in THF, 25 mmol, 17 ml) was added to a suspension of CuI (12.5 mmol, 2.4 g) in THF (10 ml) at -23°C. After the whole was stirred for 0.5 h, tributylstannyloxirane (10 mmol, 3.3 g) in THF (10 ml) was added dropwise at -78°C. The resulting mixture was warmed up to 0°C gradually, and stirred for 3 h. Aqueous work-up and purification by silica gel chromatography gave 2-tributylstannyl-3-buten-1-ol (2.9 g) in 80% yield: S. Matsubara and K. Utimoto, unpublished results.
12. A possible mechanism is the addition of perfluoroalkyl radical to alkenylstannane followed by the elimination of iodotributylstannane. The role of palladium(0) in the reaction is a kind of radical initiator.[7]



Another possible one which was proposed by Stille[8] for the palladium catalyzed coupling reaction of organotin compounds with acyl chloride could be applied. Stereoselectivity of the reaction (run 1 and 3 in Table), however, can not be explained by the latter.

(Received in Japan 27 June 1987)