

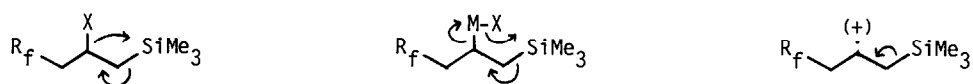
TRANSITION-METAL COMPLEX CATALYZED POLYFLUOROALKYLATION. II. NOVEL AND CONVENIENT ROUTE TO 3-POLYFLUOROALKYLPROP-1-ENES THROUGH THE REACTION OF POLYFLUOROALKYL HALIDES WITH ALLYLSILANES

Takamasa Fuchikami and Iwao Ojima¹

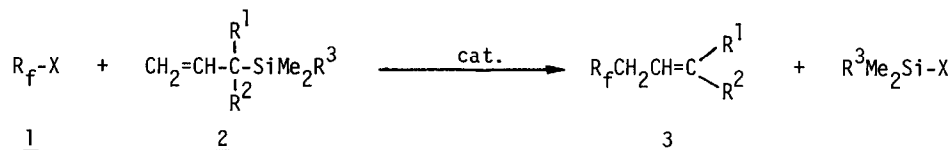
Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

Summary: The reactions of polyfluoroalkyl halides with allylsilanes catalyzed by iron or ruthenium carbonyl complexes give 3-polyfluoroalkylprop-1-enes in good yields under mild conditions.

Recently, it has been shown that allylsilanes are versatile reagents for introducing allylic moieties in organic synthesis.² In the course of our study on the polyfluoroalkylation of carbon-carbon multiple bonds catalyzed by Group VIII transition-metal complexes,³ we looked at the reactivity of allyltrimethylsilane toward the polyfluoroalkylation in the hope of exploiting new and convenient method for the allylation of polyfluoroalkyl halides, which gives synthetic building blocks for a variety of organofluorine compounds. If the reaction would proceed in a manner similar to that with normal alkenes,³ 2-halo-3-polyfluoroalkylpropyltrimethylsilane should be obtained. However, it was anticipated that the reaction would give 3-polyfluoroalkylprop-1-ene through the elimination of halotrimethylsilane i) from initially formed 2-halo-3-polyfluoroalkylpropyltrimethylsilane under the given reaction conditions or ii) via 3-polyfluoroalkyl-1-trimethylsilylprop-2-ylmetal halide, or through the elimination of trimethylsilyl radical (or ion) via 3-polyfluoroalkyl-1-trimethylsilylprop-2-yl radical (or ion). In fact, we found that the reaction of polyfluoroalkyl iodides or bromides with allyl-



trimethylsilane catalyzed by $\text{Fe}_3(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{12}$ gave 3-polyfluoroalkylprop-1-ene exclusively in high yields: No simple adducts were obtained at all. Accordingly, the reaction has turned out to serve as novel and convenient method for the allylation of polyfluoroalkyl halides.



Typically, a mixture of polyfluoroalkyl halide (1) (2.0 mmol), allylsilane (2) (2.0 mmol) and $\text{Fe}_3(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{12}$ ($0.6\text{-}4.0 \times 10^{-2}$ mmol) was sealed in a Pyrex tube (5 ml) and heated at 60°C for 3-20 h with stirring. Then the reaction mixture was submitted to distillation or preparative GLC to give 3-polyfluoroalkylprop-1-ene (3) and halosilane. Results are summarized in Table 1.

Table 1. Reaction of Polyfluoroalkyl Halides with Allylsilanes

Entry	R _f	X	R ¹	R ²	R ³	Cat. ^a (mol%)	EA ^b (mol%)	Temp. (°C)	Time (h)	Product ^c (% yield)
1	C ₃ F ₇	I	H	H	Me	Fe ₃ (2.0)		60	12	<u>3a</u> (80)
2	C ₈ F ₁₇	I	H	H	Me	Ru ₃ (0.3)		60	19	<u>3b</u> (71)
3	CF ₂ CF ₂ Br	I	H	H	Me	Fe ₃ (1.3)	(12)	60	3	<u>3c</u> (85)
4	CFC1CF ₂ Cl	I	H	H	Me	Fe ₃ (1.3)	(12)	60	4	<u>3d</u> (85)
5	CFHCF ₂ Cl	I	H	H	Me	Fe ₃ (1.3)	(12)	60	3	<u>3e</u> (75)
6	CFC1CF ₂ Br	Br	H	H	Me	Ru ₃ (0.3)		60	6	<u>3f</u> (59)
7	CF(CF ₂ Br)CF ₃	Br	H	H	Me	Fe ₃ (1.3)	(12)	60	20	<u>3g</u> (40)
8	CFC1CF ₂ Cl	I	H	CH ₂ CF ₃	Me	Fe ₃ (2.0)	(15)	60	2	<u>3h</u> (85)
9	CFC1CF ₂ Cl	I	H	Me	H	Ru ₃ (0.6)		60	3	<u>3i</u> (82)
10	CFC1CF ₂ Cl	I	H	H	Me	hv ^d		0	3	<u>3d</u> (65)
11	CFC1CF ₂ Cl	I	H	H	Me	AIBN ^e (12)		80	8	<u>3d</u> (40)

^a Fe₃=Fe₃(CO)₁₂, Ru₃=Ru₃(CO)₁₂. ^b EA=ethanolamine. ^c Determined by GLC. ^d Irradiated externally with 400 W high-pressure Hg lamp. ^e AIBN=azobisisobutyronitrile.

In order to elucidate the regioselectivity of the reaction, we carried out the reaction by employing 1,2-dichloro-1-iodo-1,2,2-trifluoroethane as polyfluoroalkyl halide and 1-(2,2,2-trifluoroethyl)prop-2-enyltrimethylsilane⁴ and 1,1-dimethylprop-2-enyldimethylsilane⁵ as allylsilane. Then, 6,7-dichloro-1,1,1,6,7,7-hexafluorohept-3-ene (3h)⁶ and 5,6-dichloro-2-methyl-5,6,6-trifluorohex-2-ene (3i)⁷ were obtained in high yields (Entries 8 and 9): The formation of the other isomer was not observed by ¹H and ¹⁹F NMR and GLC analyses at all in each case. The results clearly indicate that the polyfluoroalkylation of allylsilane takes place exclusively at the γ-position of allylsilane.

We also found that this type of reaction was effected by photo-irradiation (Entry 10) or a radical initiator (Entry 11) though the yield of 3d was lower than that achieved by Fe₃(CO)₁₂-catalyzed reaction (Entry 4).

Further studies on the mechanism as well as application of the present reaction are actively in progress.

REFERENCES AND NOTES

1. Present address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, USA.
2. For recent reviews: (a) W. P. Weber, "Silicon Reagents for Organic Synthesis", Springer-Verlag, Berlin, 1983, pp 173-205; (b) H. Sakurai, *Pure & Appl. Chem.*, **54**, 1 (1982).
3. T. Fuchikami and I. Ojima, *Tetrahedron Lett.*, the preceding paper in this issue.
4. This allylsilane was prepared by CuI-catalyzed coupling⁸ of vinyl bromide with 3,3,3-trifluoro-1-trimethylsilylpropylmagnesium iodide.
5. A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 2589 (1978).
6. Compound 3h (mixture of E and Z isomers): ¹H NMR (CDCl₃:TMS): δ 2.6-3.4(m, 4H), 5.5-6.1(m, 2H). ¹⁹F NMR (CDCl₃:CFCl₃): δ -66.5, -66.9(t, J=10.5Hz, 3F), -67.0, -67.1(bd, J=9.5Hz, 2F), -120.2(m, 1F). Elemental analysis: Calcd. for C₇H₉Cl₂F₆: C, 30.57; H, 2.20. Found: C, 30.31; H, 2.38.
7. Compound 3i: ¹H NMR (CDCl₃:TMS): δ 1.17(bs, 3H), 1.24(bs, 3H), 2.2-3.3(m, 4H), 3.68(s, 3H), 4.6(m, 1H). ¹⁹F NMR (CDCl₃:CFCl₃): δ -66.6(d, J=10Hz, 2F), -118.9(m, 1F). Elemental analysis: Calcd. for C₇H₉Cl₂F₃: C, 38.04; H, 4.10. Found: C, 37.96; H, 4.16.
8. J. F. Normant, A. Commerçon, G. Cahiez and J. Villieras, *C. R. Acad. Sci., Paris, (C)* **278**, 967 (1974).

(Received in Japan 12 September 1983)