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Transition-Metal Complex Catalyzed Polyfluoroalkylation. A Facile Synthesis of Fluorine-Containing Oxiranes and Enynes

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Palladium-catalyzed reaction of polyfluoroalkyl halides with allylic alcohols in the presence of potassium carbonate gives polyfluoroalkylmethyl-substituted oxiranes directly. Perfluoroalkyl-substituted enynes can be also prepared from perfluoroalkyl iodides and terminal alkynes under similar conditions.

Introduction of polyfluoroalkyl groups into organic molecules is one of the most important and effective methods for the synthesis of a variety of organofluorine compounds.[1)] We have already reported that Group VIII transition-metal carbonyl complexes effectively catalyze the addition of polyfluoroalkyl halides to alkenes and alkynes under very mild conditions.[2)] Since then, a variety of transition-metal complexes have been proved to have the similar catalytic activities.[3)] In these reactions, one can easily suppose the presence of intermediately formed alkyl- and alkenyl-transition metal complexes **A**, which undergo reductive elimination of alkyl or alkenyl halides (**1**), respectively, to regenerate low-valent active species. If a second reagent can trap these intermediates **A** prior to the reductive elimination, a variety of further functionalizations such as coupling, nucleophilic substitution, and carbonylation may be possible *via* these intermediates **A**. Here, we wish to report a facile synthesis of fluorine-containing oxiranes or enynes from polyfluoroalkyl halides and allylic alcohols or terminal alkynes using palladium catalyst.

$$R_f\text{-}X + C\equiv C + \textbf{Met} \longrightarrow \underset{\textbf{A}}{[R_f\text{-}C{=}C\text{-}\textbf{Met}\text{-}X]} \longrightarrow \underset{\textbf{1}}{R_f\text{-}C{=}C\text{-}X} + \textbf{Met}$$

Recently, similar key intermediates have been proposed by Nagashima, Sato, and Tsuji in the palladium-catalyzed reaction of carbon tetrachloride or bromotrichloromethane with allylic alcohols in the presence of K_2CO_3 to give rise to the formation of γ,γ,γ-trichloroketones through the subsequent β-hydride elimination from these intermediates.[4)] As already reported by one of us,[2)] perfluoroalkyl halides add to allylic alcohols with terminal double bonds in the presence of catalytic amounts of iron, cobalt, or ruthenium carbonyl complex to give 3-perfluoroalkyl-2-iodopropanols in good yields, even in the presence of amine. Our attempts to obtain β-perfluoroalkyl-substituted ketones or aldehydes from perfluoroalkyl iodides and allylic alcohols using $Fe_3(CO)_{12}$ catalyst under similar conditions to above, resulted in the formation of γ-perfluoroalkyl-substituted allylic alcohols in low yields (≈20 %) as a main product with the absence of simple adducts (**1**). On the other hand, perfluoroalkylmethyl-substituted oxiranes (**2**) in place of the expected ketones or aldehydes were obtained in good yields on using $PdCl_2(PPh_3)_2$ as a catalyst. A variety of polyfluoroalkyl halides and allylic alcohols with terminal double bonds were employable as substrates. Results are summarized in Table 1. No stereoselective formations of *cis*- and *trans*-oxiranes were observed in the present reactions.[5] Under our conditions, detectable amounts of neither fluorine-containing ketones nor aldehydes were formed. Moreover, the fact that the simple adducts (**1**), 3-polyfluoroalkyl-2-halopropanols, couldn't be detected by GLC at any stages of these reactions[6] suggests us the oxiranes (**2**) may be initial products in our catalytic systems.

Similarly, perfluoroalkylmethyl-substituted aziridines (**3**) can be prepared in

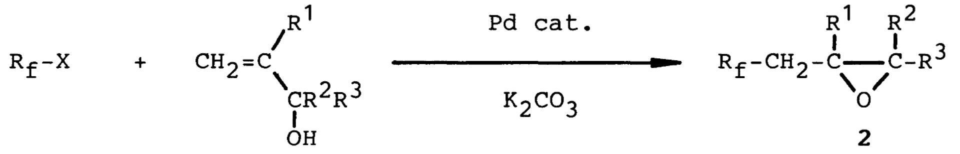
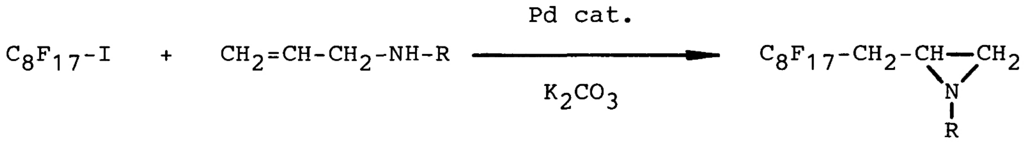


Table 1. Reaction of Polyfluoroalkyl Halides with Allylic Alcohols[a)]

Run	R_f	X	R^1	R^2	R^3	Solvent	Temp/°C	Time/h	Yield of 2/%
1	n-C_8F_{17}	I	H	H	H	EtOH	80	3	70
2			H	H	H	CH_3CN	80	6	75
3			H	H	CH_3	EtOH	80	6	69
4			H	H	CH_3	EtOH	50	18	71
5			H	CH_3	CH_3	EtOH	80	6	79
6			CH_3	H	C_2H_5	EtOH	80	6	56
7			H	H	n-C_6H_{13}	EtOH	80	6	70
8	CF_3	I	H	H	n-C_6H_{13}	EtOH	80	18	63
9	C_2F_5	I	H	H	n-C_6H_{13}	EtOH	80	18	71
10	n-C_3F_7	I	H	H	n-C_6H_{13}	EtOH	80	6	77
11	i-C_3F_7	I	H	H	n-C_6H_{13}	EtOH	80	18	30
12	n-C_4F_9	I	H	H	n-C_6H_{13}	EtOH	80	7	72
13	n-C_6F_{13}	I	H	H	n-C_6H_{13}	EtOH	80	7	74
14	CF_2BrCF_2	I	H	H	n-C_6H_{13}	EtOH	80	12	47
15	$CF_2ClCFCl$	I	H	H	n-C_6H_{13}	EtOH	80	12	56
16	$CF_2BrCFCl$	Br	H	H	n-C_6H_{13}	EtOH	80	9	27

a) All reactions were run with polyfluoroalkyl halide (0.5-3.0 mmol: 0.8-1.0 M), allylic alcohol (1.1-2.0 equiv.), K_2CO_3 (1.0-2.0 equiv.), and $PdCl_2(PPh_3)_2$ (1.4-2.8 mol%).

moderate yields from perfluorooctyl iodide and allylic amines.



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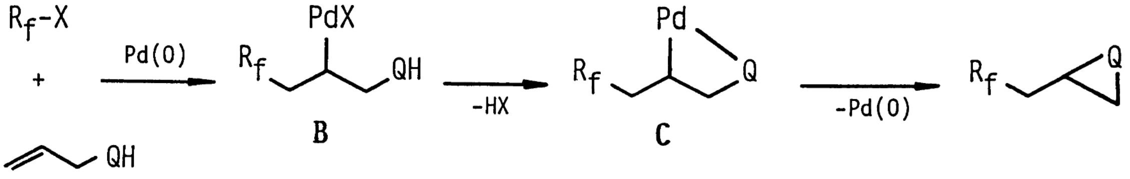
R=H (35%); R=Ph (41%)

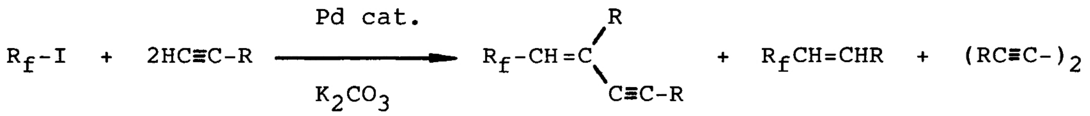
The formation of these products can be rationally explained by taking account of intermediately formed palladium complex **B**, which undergoes intramolecular nucleophilic attack of oxygen (or nitrogen) atom to form palladia-oxa(aza)cyclobutane intermediates **C**, followed by reductive elimination giving the products. The reason why β-elimination of metal-hydride species from the intermediates **B** is negligible pathway in our reactions is not clear now. Some interactions between palladium center and fluorine atom(s) at γ- or δ-position may play an important role to prevent the intermediates **B** from β-hydride elimination.



Q = O, NR

The carbon-carbon bond-forming reaction *via* alkenyl-palladium intermediates **A**, derived from perfluoroalkyl iodides, alkynes, and low-valent palladium species, was turned out to be also possible. When perfluorooctyl iodide and 1-hexyne were heated at 80 °C in ethanol in the presence of $PdCl_2(PPh_3)_2$ as a catalyst and base such as K_2CO_3 or Et_3N, 1-perfluorooctyl-2-butyl-1-octen-3-yne (**4a**) was obtained in 23 to 27% yield with 1-perfluorooctyl-1-hexene (**5a**) (14-16%) and dodeca-5,7-diyne (**6a**) (3-5%). The addition of CuI as co-catalyst$^{7)}$ increases the yield of the desired enyne (**4a**) (36-41%), but homo-coupling product **6a** is serious by-product(29-46%) in ethanol. The best results were obtained by using a mixed solvent of $CHCl_3$-EtOH (5/1). The reaction of trimethylsilylacetylene also gave us perfluoroalkyl-substituted 2,4-bis(trimethylsilyl)-1-buten-3-yne (**4b**) in 70% yield. As trimethylsilyl group can be easily removed by the attack of fluoride ion, this compound may be a useful monomer for functional fluoropolymers as well as a building block for organic syntheses.

The reaction described here seems to proceed through the alkenyl-palladium intermediates **A**, similar to those in the palladium-catalyzed coupling reaction of aryl or vinyl halides with alkynes.$^{7,8)}$



$$R_f\text{-I} + 2HC{\equiv}C\text{-R} \xrightarrow[K_2CO_3]{\text{Pd cat.}} R_f\text{-CH=C}\begin{matrix}R\\ \\ C{\equiv}C\text{-R}\end{matrix} + R_fCH{=}CHR + (RC{\equiv}C\text{-})_2$$

4 **5** **6**

a: $R_f = n\text{-}C_8F_{17}$, $R = n\text{-}C_4H_9$; **b**: $R_f = n\text{-}C_3F_7$, $R = SiMe_3$

Table 2. Reaction of Perfluoroalkyl Iodides with Terminal Alkynes[a)]

R_f	R	Co-cat. (mol%)	Base	Solvent	Temp/°C	Time/h	Yield/% **4**	**5**	**6**
$n\text{-}C_8F_{17}$	$n\text{-}C_4H_9$	---	Et_3N	EtOH	80	3	27	14	3
		---	K_2CO_3	EtOH	80	3	23	16	5
		CuI(4.2)	Et_3N	EtOH	80	3	36	15	46
		CuI(4.2)	K_2CO_3	EtOH	80	3	41	13	7
		CuI(4.2)	K_2CO_3	$CHCl_3$-EtOH[b)]	50	17	74	3	7
$n\text{-}C_3F_7$	$SiMe_3$	CuI(4.2)	K_2CO_3	$CHCl_3$-EtOH[b)]	50	17	70	nd[c)]	nd[c)]

a) All reactions were run with perfluoroalkyl iodide (0.5 mmol; 1 M), alkyne (3.0 equiv.), base (2.0 equiv.), and $PdCl_2(PPh_3)_2$ (2.8 mol%). b) A mixed solvent of $CHCl_3$-EtOH (5:1) was used. c) Not determined.

Further functionalizations *via* the key intermediates **A** and applications for the synthesis of useful organofluorine compounds as well as mechanistic studies are now in progress.

References

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5) For example, the ratio of *cis* and *trans* isomers was found to be 54:46 by GLC analysis in Run 3 (Table 1).
6) Palladium catalyzed addition of perfluoroalkyl iodides to carbon-carbon double bond of allylic alcohols under neutral conditions is very fast: For example, a 5-minute reaction of perfluorooctyl iodide and allyl alcohol *without* K_2CO_3 in EtOH under similar conditions using $Pd(PPh_3)_4$ as catalyst gave 62% isolated yield (78% conversion) of 3-perfluorooctyl-2-iodopropanol.
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