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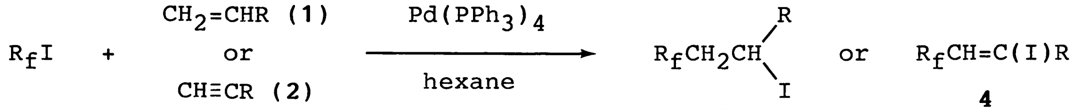
New Efficient Palladium-Catalyzed Perfluoroalkylation of Carbon-Carbon Multiple Bonds with F-Alkyl Iodides. An Expedient Route to F-Alkylated Alkyl and Alkenyl Iodides

Takashi ISHIHARA,* Manabu KUROBOSHI, and Yoshiji OKADA
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606

A variety of alkenes and alkynes efficiently undergo the perfluoroalkylation with F-alkyl iodides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in hexane to give good yields of the corresponding F-alkylated alkyl and alkenyl iodides, respectively.

The perfluoroalkylation of a carbon-carbon multiple bond is an interesting and valuable reaction in organic synthesis. The methods reported so far for such a transformation involve a photo-irradiated,$^{1)}$ radical-initiated,$^{2)}$ thermal,$^{3)}$ and electrochemical reaction$^{4)}$ of F-alkyl halides with alkenes or alkynes. These methods, however, do not necessarily give satisfactory yields of the products, and often suffer from side reactions. Some transition-metal carbonyl complexes have recently proved to be effective for this type of reaction.$^{5)}$ Still of much importance is to develop a novel method for introducing an F-alkyl group to organic molecules.

In this communication is disclosed the first example of a palladium complex-catalyzed addition reaction of F-alkyl iodides to the carbon-carbon multiple bond of various alkenes and alkynes under mild conditions. This reaction can serve as a simple, effective method for the synthesis of F-alkylated alkyl or alkenyl iodides in good yields.



$$R_fI \; + \; \begin{array}{c} CH_2{=}CHR\ (\mathbf{1}) \\ \text{or} \\ CH{\equiv}CR\ (\mathbf{2}) \end{array} \xrightarrow[\text{hexane}]{Pd(PPh_3)_4} R_fCH_2CH(R)I \quad \text{or} \quad R_fCH{=}C(I)R$$

3 **4**

When F-alkyl iodide was treated with alkene (**1**) or alkyne (**2**) (1.0-1.2 equiv.) in the presence of a catalytic amount (5-10 mol%) of tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] in hexane, 1-F-alkyl-2-iodoalkane (**3**) or 1-F-alkyl-2-iodo-1-alkene (**4**) was obtained$^{6)}$ in good yield, respectively. The reaction did not occur at all in tetrahydrofuran, 1,2-dichloroethane, nor in benzene. Out of the catalysts examined such as $Pd(PPh_3)_4$, dichlorobis(triphenylphosphine)palladium(II), and palladium(II) chloride, only $Pd(PPh_3)_4$ was effective for the present reaction. The results are summarized in Table 1. Various terminal alkenes and alkynes were regioselectively perfluoroalkylated with F-alkyl iodides by the aid of the palladium catalyst. The hydroxyl, carbonyl, and trimethylsilyl

Table 1. Pd-Catalyzed reaction of *F*-alkyl iodides with alkenes and alkynes[a)]

R_f	Alkene or alkyne 1 or 2	Product 3 or 4	Yield[b)] %	Isomer ratio[b)] E/Z
$CF_3(CF_2)_2$	$CH_2=C(C_2H_5)\text{-}n\text{-}C_4H_9$	**3a**	78	-
	$CH_2=CH(CH_2)_2OH$	**3b**	65[c)]	-
	$CH\equiv C\text{-}n\text{-}C_6H_{13}$	**4a**	62	86/14
	$CH\equiv CPh$	**4b**	57	96/4
$CF_3(CF_2)_3$	$CH_2=CH\text{-}n\text{-}C_6H_{13}$	**3c**	78[c)]	-
	$CH_2=C(C_2H_5)\text{-}n\text{-}C_4H_9$	**3d**	67	-
	$CH_2=CHCH_2OH$	**3e**	55	-
	$CH_2=CH(CH_2)_2OH$	**3f**	60	-
	$CH_2=CH(CH_2)_2COCH_3$	**3g**	69[c)]	-
	$CH_2=CHCH_2Si(CH_3)_3$	**3h**	68	-
	$CH\equiv C\text{-}n\text{-}C_6H_{13}$	**4c**	66[c)]	92/8
	$CH\equiv CPh$	**4d**	67	96/4
	$CH\equiv CSi(CH_3)_3$	**4e**	68	67/33
$CF_3(CF_2)_5$	$CH_2=CH\text{-}n\text{-}C_6H_{13}$	**3i**	73[c)]	-
	$CH_2=CH(CH_2)_2OH$	**3j**	71[c)]	-
	$CH_2=CHCH_2Si(CH_3)_3$	**3k**	78[c)]	-
	$CH\equiv C\text{-}n\text{-}C_4H_9$	**4f**	69	91/9
	$CH\equiv C\text{-}n\text{-}C_6H_{13}$	**4g**	71	91/9
	$CH\equiv CSi(CH_3)_3$	**4h**	76	72/28

a) The reaction of **1** was performed at ambient temperature for 3-6 h by using 5 mol% of $Pd(PPh_3)_4$. The reaction of **2** was run in the presence of 10 mol% of $Pd(PPh_3)_4$ at 60-67 °C for 24 h. b) Determined by ^{19}F NMR. c) Isolated yield.

groups in **1** or **2** were tolerant of the reaction. The reaction of internal alkynes such as 2-hexyne and 4-octyne proceeded under the same conditions to give 50-60% yields of the products.[6,7] In the case of cyclohexene and *cis*- and *trans*-3-hexene, the corresponding *F*-alkylated iodides were obtained[6] in 40-50% yields under forced conditions (67 °C, 24 h). The addition of *p*-dinitrobenzene as a radical scavenger retarded the reaction. This fact suggests that the present reaction occurs *via* a free radical process in nature.

Further studies on synthetic applications of this reaction as well as its mechanism are now in progress.

References

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