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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

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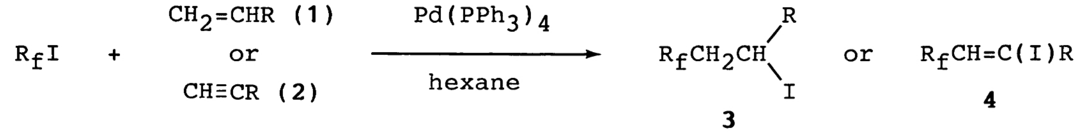
A variety of alkenes and alkynes efficiently undergo the perfluoroalkylation with F-alkyl iodides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in hexane to give good yields of the corresponding F-alkylated alkyl and alkenyl iodides, respectively.

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 reaction4) 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.



$$R_fI + \begin{matrix} CH_2{=}CHR\ (\mathbf{1}) \\ \text{or} \\ CH{\equiv}CR\ (\mathbf{2}) \end{matrix} \xrightarrow[\text{hexane}]{Pd(PPh_3)_4} \underset{\mathbf{3}}{R_fCH_2CH(R)I} \text{ or } \underset{\mathbf{4}}{R_fCH{=}C(I)R}$$

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 obtained6) 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)-n-C_4H_9	3a	78	-
	CH_2=CH(CH_2)$_2$OH	3b	65[c)]	-
	CH≡C-n-C_6H_{13}	4a	62	86/14
	CH≡CPh	4b	57	96/4
$CF_3(CF_2)_3$	CH_2=CH-n-C_6H_{13}	3c	78[c)]	-
	CH_2=C(C_2H_5)-n-C_4H_9	3d	67	-
	CH_2=CHCH_2OH	3e	55	-
	CH_2=CH(CH_2)$_2$OH	3f	60	-
	CH_2=CH(CH_2)$_2$COCH_3	3g	69[c)]	-
	CH_2=CHCH_2Si(CH_3)$_3$	3h	68	-
	CH≡C-n-C_6H_{13}	4c	66[c)]	92/8
	CH≡CPh	4d	67	96/4
	CH≡CSi(CH_3)$_3$	4e	68	67/33
$CF_3(CF_2)_5$	CH_2=CH-n-C_6H_{13}	3i	73[c)]	-
	CH_2=CH(CH_2)$_2$OH	3j	71[c)]	-
	CH_2=CHCH_2Si(CH_3)$_3$	3k	78[c)]	-
	CH≡C-n-C_4H_9	4f	69	91/9
	CH≡C-n-C_6H_{13}	4g	71	91/9
	CH≡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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