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Transition-Metal Complex Catalyzed Perfluoroalkylation. A Facile Synthesis of Fluorine-Containing Esters by Carbo-Carbonylation of Alkynes and Alkenes

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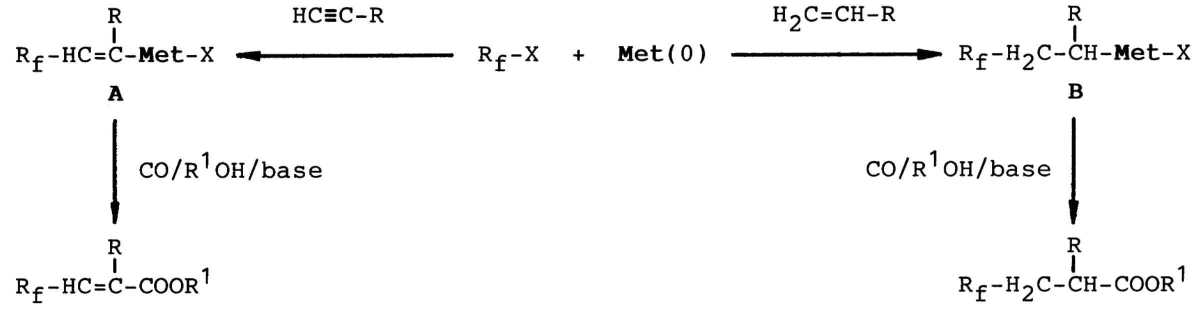
Palladium-catalyzed reaction of perfluoroalkyl iodides with terminal alkynes or alkenes in alcohols under carbon monoxide pressure in the presence of potassium carbonate directly gives β-perfluoroalkyl-substituted alkenoates or alkanoates, respectively.

Fluorine-containing carbonyl compounds are versatile building blocks for the synthesis of useful organofluorine compounds.[1)] We have already shown that Group VIII transition-metal catalyzed carbonylations of fluorine-containing terminal olefins are one of the most convenient and efficient methods for their preparations.[2)] However, these carbonylations were difficult to apply to the internal ones because of low reactivities and non-regioselectivities. Recently, we have found that transition-metal complexes effectively catalyze the addition of polyfluoroalkyl halides to terminal alkynes and alkenes,[3-5)] in which β-polyfluoroalkyl-substituted alkenyl- and alkyl-transition-metal species (**A** and **B**, Scheme 1) may be formed intermediately by carbo-metallation to alkynes and alkenes, respectively. If carbon monoxide can easily insert into the carbon-metal bonds of these intermediates (**A** and **B**) prior to undergoing β-hydride elimination or reductive elimination of halides, β-perfluoroalkyl substituted alkenoates and alkanoates are expected to be formed in alcohols by "carbo-carbonylation reaction"[6)] of alkynes and alkenes, respectively (Scheme 1).



Scheme 1.

Among Group VIII transition-metal complexes examined as a catalyst, we found that $PdCl_2(PPh_3)_2$ was the most effective catalyst for carbo-carbonylation of 1-alkynes (**1**) with perfluoroalkyl iodides in alcohols in the presence of K_2CO_3 as base at 80 °C to give β-perfluoroalkyl-substituted acrylates (**3**) in 49-58% yields, in addition to 1-perfluoroalkyl-1-alkenes (**5**) (9-14%) (Eq. 1). The representative results are listed in Table 1. Other transition-metal complexes such as $PtCl_2(PPh_3)_2$, $NiCl_2(PPh_3)_2$, $RhCl(CO)(PPh_3)_2$, and $Rh_6(CO)_{16}$ showed no ability for this carbonylation, though $Ru_3(CO)_{12}$ afforded only 6% yield of the desired ester **3a** under the same reaction conditions as Run 1. We also observed that K_2CO_3 is the best base,[7] and the esters (**3**) were obtained in lower yields in case of triethylamine or pyridine was employed instead of K_2CO_3. It is noteworthy that the present carbonylation smoothly proceeds at normal pressure of carbon monoxide, and the simple adduct,[5] 1-perfluoroalkyl-2-iodo-1-alkene, couldn't be detected by GLC analysis at any stages of these reactions. Perfluoroalkyl groups attach exclusively at terminal carbon atom of 1-alkynes, and (*E*)-isomers were preferentially formed except for 3,3-dimethyl-1-butyne.[8] The formation of olefins **5** suggests that initial stage of these reaction (carbo-metallation step) may involve some radical character.[6]

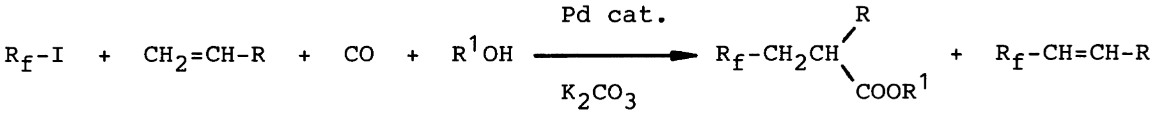
$$R_f\text{-I} \;+\; \underset{\mathbf{1}}{HC{\equiv}CH\text{-}R} \;+\; CO \;+\; R^1OH \;\xrightarrow[K_2CO_3]{\text{Pd cat.}}\; \underset{\mathbf{3}}{R_f\text{-CH=CR-COOR}^1} \;+\; \underset{\mathbf{5}}{R_f\text{-CH=CH-R}} \qquad (1)$$

Table 1. Carbo-carbonylation of Alkynes and Alkenes with Perfluoroalkyl Iodides[a]

Run	R_f	**1** or **2** (R)	R^1	Temp/°C	Time/h	Yield/% **3** (E/Z)[b] or **4**	 **5**
1	C_8F_{17}	**1** (n-C_4H_9)	C_2H_5	80	4.5	**3a:** 52(86/14)	**5a:** 12
2		**1** (n-C_4H_9)	n-C_3H_7	80	7	**3b:** 58(83/17)	**5a:** 12
3		**1** (n-C_4H_9)	i-C_4H_9	80	6	**3c:** 58(86/14)	**5a:** 9
4		**1** (t-C_4H_9)	i-C_4H_9	80	3	**3d:** 44(0/100)	**5b:** 13
5		**2** (n-C_4H_9)	C_2H_5	80	12	**4a:** 67	**5a:** 3
6		**2** (n-C_4H_9)	n-C_3H_7	100	24	**4b:** 40	**5a:** 11
7		**2** (n-C_4H_9)	i-C_4H_9[c]	100	24	**4c:** 53	**5a:** 8
8		**2** (n-C_6H_{13})	n-C_3H_7	100	24	**4d:** 60	**5c:** nd[d]
9		**2** (n-C_8H_{17})	C_2H_5[c]	100	24	**4e:** 41	**5d:** nd[d]
10	C_7F_{15}	**1** (i-C_5H_{11})	n-C_3H_7	80	4	**3e:** 55(86/14)	**5e:** 14
11	C_4F_9	**1** (n-C_6H_{13})	C_2H_5	80	4	**3f:** 49(89/11)	**5f:** nd[d]
12		**2** (i-C_5H_{11})	n-C_3H_7	100	24	**4f:** 48	**5g:** nd[d]

a) All reactions were carried out with perfluoroalkyl iodide (0.5 mmol; 0.22 M), alkene or alkyne (0.86 mmol), K_2CO_3 (0.5 mmol), and $PdCl_2(PPh_3)_2$ (1-2 mol%) in alcohol, under normal pressure of CO for alkyne or under 30 atm of CO for alkene. b) The ratios were determined by ^1H, ^{19}F, and ^{13}C NMR. c) Heptane was used as co-solvent. d) Not determined.

Similarly, the carbo-carbonylation of terminal olefins takes place under some elevated pressure of carbon monoxide (10-30 atm), and β-perfluoroalkyl-substituted propionates (**4**) were obtained directly from perfluoroalkyl iodides, 1-alkenes (**2**) and alcohols using $PdCl_2(PPh_3)_2$ as a catalyst (Eq. 2). The by-product was found to be 1-perfluoroalkyl-1-alkenes (**5**), and no other isomers nor perfluoroalkyl-containing alkanes could be observed by spectroscopic analyses. The satisfactory results were obtained using K_2CO_3 as base in alcohol or alcohol-heptane solution as shown in Table 1. In this carbonylation, $PtCl_2(PPh_3)_2$ and $Co_2(CO)_8$ also exhibit moderate catalytic activities, and 30-40% yields of **4a** were formed under the same reaction conditions as Run 5.

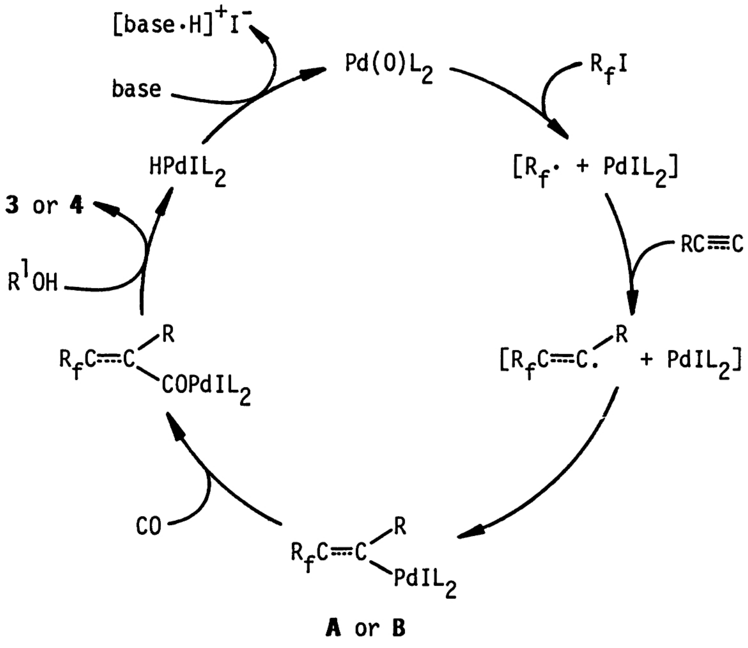


$$R_f\text{-I} + CH_2=CH\text{-R} + CO + R^1OH \xrightarrow[K_2CO_3]{\text{Pd cat.}} R_f\text{-}CH_2CH\begin{matrix}R\\ \\ COOR^1\end{matrix} + R_f\text{-}CH=CH\text{-}R \qquad (2)$$

2 **4** **5**

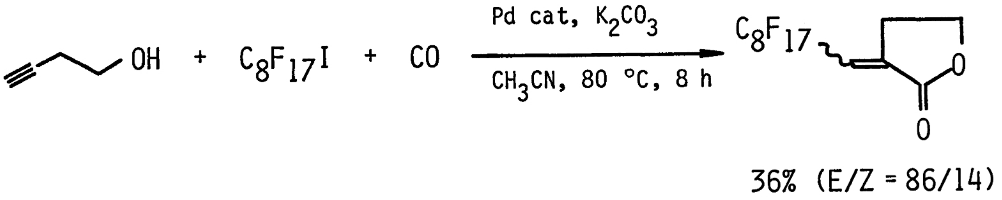
When the above reaction (Eq. 2) was carried out under atmospheric pressure of CO or Ar in the presence of palladium catalyst, the simple adduct,[5] 1-perfluoroalkyl-2-iodoalkane, was formed *ca.* 70% yield within 10 min as initial product, and it successively underwent the dehydroiodination to olefin **5** by the action of K_2CO_3. On the other hand, the simple adduct couldn't be detected in the course of these reactions under pressurerized conditions (>10 atm of CO).

Based on the results obtained here, the present carbo-carbonylation may be explained by a mechanism (Scheme 2) similar to that proposed by Tsuji *et al.*[6] The coordination of CO to palladium center in place of PPh_3 may prevent the intermediates **A** and **B** from undergoing the reductive elimination of the iodides (simple adducts), and facilitate the formation of acyl complexes, and weak coordination of fluorine atom(s) to a vacant site of palladium center may also play a role to impede the β-hydride elimination from the intermediates **B**.

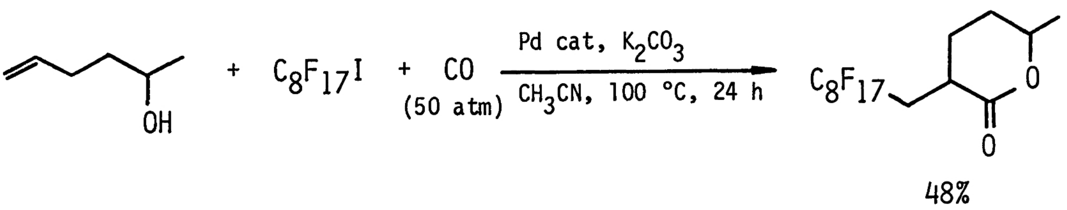


Scheme 2.

The present carbonylation was applicable for the preparation of fluorine-containing lactones. α-Perfluoroalkylmethylidene-γ- and δ-lactones were formed by using 3-butyn-1-ol and 4-pentyn-1-ol, respectively, in acetonitrile as solvent. Similarly, homoallyl and bishomoallyl alcohols gave the corresponding lactones under pressurized conditions. Examples are shown in Eqs. 3 and 4.



(3)



(4)

Further applications and precise mechanistic studies of these carbo-carbonylation reactions are currently in progress.

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6) This type of carbonylation of olefins has been reported by J. Tsuji *et al.* using carbon tetrachloride: See, T. Susuki and J. Tsuji, Tetrahedron Lett., 1968, 913; J. Org. Chem., 35, 2982 (1970); J. Tsuji, K. Sato, and H. Nagashima, Tetrahedron Lett., 23, 893 (1982); Tetrahedron, 41, 5003 (1985).

7) Most of K_2CO_3 was insoluble in the present reaction conditions listed in the Table 1. When methanol was used as a solvent instead of ethanol in Run 1, where K_2CO_3 was completely dissolved, 1-perfluorooctyl-2-butyl-1-octene-3-yne was formed as a main product in 20% yield in addition to **3** (2%) and **5** (7%).

8) In the persistent vinyl radicals sterically protected by bulky groups such as *tert*-butyl or trimethylsilyl, the two bulky substituents have been proposed to take up a *trans*-configuration with respect to one another. See, D. Griller, J. W. Cooper, and K. U. Ingold, J. Am. Chem. Soc., 97, 4269 (1975).

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