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PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS BETWEEN ALLYL, VINYL OR ARYL HALIDE AND PERFLUOROALKYL IODIDE WITH ZINC AND ULTRASONIC IRRADIATION

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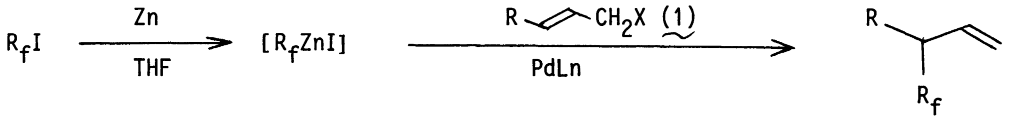
The reactions of perfluoroalkyl iodides with allyl, vinyl or aryl halides with ultrasonically dispersed zinc in the presence of palladium catalyst proceeded smoothly to give the corresponding allyl, vinyl or aryl perfluoroalkylides in a good yield.

A cross-coupling reaction of organometallic compounds and organic halides is one of the most attractive procedures in organic synthesis.[1)] in the field of fluorine chemistry, polyfluoro organic compounds have recently been attracting attentions owing to their unique properties, such as high electronegativity, stability and interfacial activity, however, little practical methods for the introduction of a perfluoroalkyl group into an organic molecule by this reaction have been known.[2-8)]

Recently, we have reported the synthesis of α-trifluoromethylcarbinols, produced by the reaction of trifluoromethylzinc iodide with carbonyl compounds with ultrasound.[9)] In our continuing studies of the introduction of perfluoroalkyl group into organic molecules with ultrasound, it now has been possible to prepare allyl, vinyl or aryl perfluoroalkylides by the palladium-catalyzed cross-coupling reaction[10)] of a perfluoroalkylzinc iodide with an allyl, vinyl or aryl halide.

Palladium-catalyzed perfluoroalkylation of allyl halides with a perfluoroalkylzinc iodide, which was formed in situ from a perfluoroalkyl iodide and zinc powder in tetrahydrofuran, proceeded smoothly. The perfluoroalkyl group was introduced regioselectively (~95%) at the γ-position of allylic derivatives(1) as shown Table II.



2

Various kinds of palladium compounds were examined as a catalyst in the case between trifluoromethylzinc iodide and cinnamyl bromide, which resulted as shown Table I. Thus, Pd(OAc)$_2$ was found to be the most suitable catalyst.

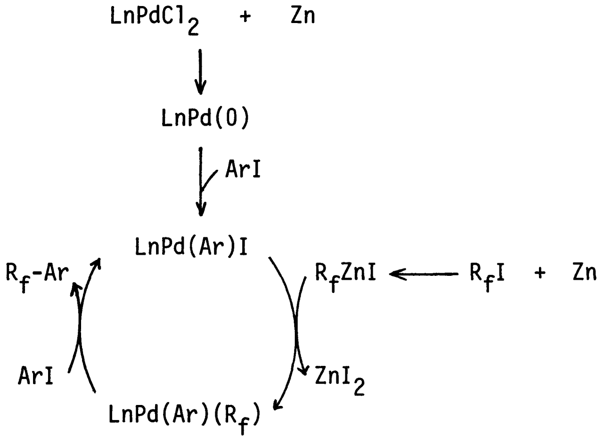
On the other hand, the perfluoroalkylation on vinylic position was achieved by using tetrakis(triphenylphosphine)palladium as a catalyst (Table II).[11-14)]

3

For the introduction of perfluoroalkyl group on the aromatic ring, the Ullmann-type reaction of R_fI with ArI using copper powder is well known,[5,6,8] however, this method is not very practical because of its sensitive operation. In contrast, ultrasonic irradiation was found to be easy to handle and to have greatly enhanced effect to promote the perfluoroalkyl organometallic reaction.

The cross-coupling reaction between a perfluoroalkylzinc iodide and an aryl halides was examined by using several types of palladium catalyst, and found that the high catalytic abilities is attained by $PdCl_2$ and $Pd(PPh_3)_2Cl_2$. Instead of $PdCl_2$, palladium black was used in the reaction of iodobenzene and heptafluoro-1-methylethylzinc iodide, furnishing (heptafluoro-1-methylethyl)-benzene in 53 % yield. This fact suggests that actual catalyst is palladium(0), which is formed from $PdCl_2$ or $Pd(PPh_3)_2Cl_2$ by Zn with ultrasound, and that it makes a catalytic reduction-oxidation cycle as shown below.

$$R_fI \quad + \quad ArI \xrightarrow[Pd(PPh_3)_2Cl_2]{Zn/THF} R_f\text{-}Ar$$



In these systems, without the aid of ultrasonic irradiation, the reaction did not proceed at all.

Based on these results, we believe that the presently reported ultrasonic irradiation promotes the introduction of a perfluoroalkyl group on allyl or vinyl position and aromatic ring, and then provides a practical one-pot synthetic method for the functionalized perfluoroalkyl compounds.

Typical procedures for the present reactions are as follows:

3-Trifluoromethyl-3-phenyl-1-propene --- A flask containing commercially available zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl iodide (2.15 g, 11 mmol), cinnamyl bromide (1.97 g, 10 mmol) and palladium acetate (0.11 g, 0.5 mmol) in tetrahydrofuran (25 ml) is irradiated in the water bath of an ultrasound laboratory cleaner (35 W, 32 KHz) for 1h. Then, the solution was poured into water and oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave 3-trifluoromethyl-3-phenyl-1-propene in 63 % yield, bp 81-83°C/25 mmHg.

TABLE I

Catalyst	Yield (%) a)
Pd(OAc)$_2$	63
PdCl$_2$	34
PdCl$_2$(PPh$_3$)$_2$	51
PdCl$_2$(PhCN)$_2$	23

a) Yields were determined by ^{19}F NMR, using PhCF$_3$ as reference.

TABLE II Perfluoroalkylation

R$_f$	Substrate	Product a)	Catalyst	React. Time(h)	Yield (%)	Bp(°C/mmHg) [Mp °C]
CF$_3$	PhCH=CHCH$_2$Br	Ph(CF$_3$)CHCH=CH$_2$ b)	Pd(OAc)$_2$	1	63	81-83/25
CF$_3$	PhCH=CHBr	PhCH=CHCF$_3$	Pd(PPh$_3$)$_4$	1	65	70-72/25(64/18) c)
CF$_3$	4-MeC$_6$H$_4$CH=CHBr	4-MeC$_6$H$_4$CH=CHCF$_3$	Pd(PPh$_3$)$_4$	1	67	[59-60] [59] c)
i-C$_3$F$_7$	PhCH=CHCH$_2$Br	Ph(C$_3$F$_7^{i}$)CHCH=CH$_2$ b)	Pd(OAc)$_2$	0.5	78	80-82/21
i-C$_3$F$_7$	PhCH=CHBr	PhCH=CHC$_3$F$_7^{i}$ b)	Pd(PPh$_3$)$_4$	1	72	75-77/24
n-C$_4$F$_9$	MeCH=CHCH$_2$Br	Me(C$_4$F$_9^{n}$)CHCH=CH$_2$ b)	Pd(OAc)$_2$	0.5	68	[81-84]
n-C$_4$F$_9$	PhCH=CHBr	PhCH=CHC$_4$F$_9^{n}$ b)	Pd(PPh$_3$)$_4$	1	62	76-78/23
CF$_3$	PhI	PhCF$_3$	PdCl$_2$(PPh$_3$)$_2$	0.5	82	101-103(101-102) d)
n-C$_3$F$_7$	PhI	PHC$_3$F$_7^{n}$	PdCl$_2$(PPh$_3$)$_2$	0.5	78	127-130
i-C$_3$F$_7$	PhI	PhC$_3$F$_7^{i}$	PdCl$_2$(PPh$_3$)$_2$	0.5	87	124-126(125) d)
i-C$_3$F$_7$	4-MeC$_6$H$_4$I	4-MeC$_6$H$_4$C$_3$F$_7^{i}$	PdCl$_2$(PPh$_3$)$_2$	0.5	81	146-148(147) d)
i-C$_3$F$_7$	2-MeC$_6$H$_4$I	2-MeC$_6$H$_4$C$_3$F$_7^{i}$	PdCl$_2$(PPh$_3$)$_2$	0.5	59	140-143(141-143) e)

a) Structures were determined by means of IR, NMR and Mass spectral data.

b) New compounds : The microanalysis was satisfactory agreement to the calculated value.(C,H,N:±0.4)

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trans-β-Trifluoromethyl styrene --- In the above reaction, zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl iodide (2.25 g, 12 mmol), trans-β-bromostyrene (1.83 g, 10 mmol) and tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) in tetrahydrofuran (25 ml) were used. Distillation gave trans-β-trifluoromethyl styrene in 65 % yield, bp 70-72°C/25 mmHg.

(Heptafluoro-1-methylethyl)benzene --- Iodobenzene (2.04 g, 10 mmol), heptafluoro-1-methylethyl iodide (2.26 g, 11 mmol), zinc powder (1.30 g, 0.02 g-atom) and $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.1 mmol) in tetrahydrofuran (25 ml) was reacted for 30 min with ultrasound, and then worked up as usual. Distillation gave (heptafluoro-1-methylethyl)benzene in 77 % yield, bp 124-126°C.

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